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MSA Research Corp.

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Package Sorption Device System Study

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Package Sorption Device System Study

by

MSA Research Corporation
Division of Mine Safety Appliances Company
Evans City, Pennsylvania 16033

Contract No. EHSD 71-2
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The report: (1) identifies and characterizes the numerous small. but objectionable. sources of gaseous pollutants; (2) ranks sources according to relative importance; (3) assesses the equipment and technology available for controlling these sources, in handbook form; (4) investigates the potential and need for development of technology and new sorbents; and (5) details research and development recommendations to improve existing devices or to develop new control methods. Emission sources amenable to control by package sorption devices contribute 15% of the total organic emissions from all sources and can be divided into two broad categories: (1) solvent-user industries that emit solvents essentially unchanged, and (2) process industries that generate pollutants by chemical, biological, or thermal reactions. Regenerative activated carbon adsorbent systems show promise for the control of pollutants from these sources, particularly at concentrations below 700 ppm. At higher concentrations, catalytic and thermal incinerators are more economical except where the would-be pollutant is a valuable solvent recoverable by the adsorbent system.

It also briefly discusses monitoring and detection methods.

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ABSTRACT

A Package Sorption Device System Study was undertaken to achieve the following objectives: (1) identify and characterize the numerous small but objectionable sources of gaseous pollutants; (2) develop ranking of sources according to relative importance; (3) assess the equipment and technology available for controlling these sources; (4) investigate the potential and need for development of new technology and new sorbents; and (5) develop detailed research and development recommendations to improve existing devices or develop new control methods. The primary products of this study are: (1) a handbook on package sorption device technology; (2) an assessment of the emissions to which this technology may be applicable; and (3) the R&D recommendations. Emission sources amenable to control by package sorption devices contribute 15% of the total organic emissions from all sources and can be divided into two broad categories: (1) solvent user industries which emit solvents essentially unchanged and (2) process industries which generate pollutants by chemical, biological or thermal reactions. Regenerative activated carbon adsorbent systems show promise for the control of pollutants from these sources, particularly at concentrations below 700 ppm. At higher concentrations, catalytic and thermal incinerators are more economical except where the would-be pollutant is a valuable solvent recoverable by the adsorbent system.

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Introduction

Objectives and Scope of Study

The package sorption device system study was conducted for the Environmental Protection Agency, under Contract Number EHS D 71-2, by MSA Research Corporation, Evans City, Pennsylvania. It deals with packaged solid sorption devices for the control of gaseous air pollutant emissions.

The study had as its primary objectives the preparation of a handbook on packaged sorption device technology, an assessment of the emissions to which the technology may be applicable, and the development of recommendations for future research and development of packaged sorption devices.

The term "packaged" connotes a size limitation on the device and thereby, also, on the size of the pollutant emission source which the device would control. For the purpose of this study, these sources are referred to as small emission sources to differentiate them from mobile and other larger stationary sources.

The term "packaged device" is loosely defined as (1) a factory assembled device transportable as a unit and/or (2) a device which can be assembled on site from a few prefabricated and readily transportable components. Such packaged devices are characterized by:

1. Small size
2. Simple, easy installation
3. Availability in essentially off-the-shelf form
4. Relatively low maintenance
5. Relatively low cost

In order to match emission volumes from the small emission sources with potential packaged control devices, the air handling capacities of various sized activated carbon solvent recovery systems were used as a measuring guide. Factory assembled solvent recovery systems that are essentially off-the-shelf sizes are commercially available up to 10,000 ft^3/min airflow capacity. Such a system would have the approximate overall length and width dimensions of 38 and 12 ft and overall height of 16 ft. Solvent recovery systems up to 50,000 ft^3/min airflow capacity are available that fit the prefabricated-component definition. Emission sources of over 50,000 ft^3/min flow rate and custom built systems to handle these higher flow rates were considered outside the scope of this study.

Although the major emphasis in this study was on sorbent devices, some necessary but limited investigations were also conducted on competing devices involving catalytic and thermal incineration.

Small emission sources, amenable to control by packaged devices, are exemplified by such sources as (1) small solvent users - dry cleaners, degreasers, and printing shops and (2) small processing and service industries - meat and fish renderers, coffee roasters, restaurants and bakeries. The general characteristics of these small sources are: (1) they are numerous, (2) the emission streams are generally of the order of 10,000 ft^3/min or less, and (3) because of their small size their polluting effects are generally felt only in local areas.

To achieve the primary objectives the study involved effort in three areas:

1. Identify the small emission sources and determine the nationwide extent and type of gaseous air pollution from these sources.

2. Evaluate the existing technology of small fixed bed sorbent and catalytic incineration package devices for the control of these sources.

3. Assess potential new technology to control pollution from these sources using fixed bed sorbent devices.

Report Content

The report consists of two parts. Part I is oriented toward the needs of management personnel in Government and industry, responsible for planning of future action in pollution control. Part II is directed more toward the needs of design engineers, fabricators, and users of control devices. Part II also contains information directed to the scientists interested in adsorption.

Part I presents the acquired information on the emission sources and recommendations for future research and development of packaged sorption devices. The information on emission sources was collected from Government publications (federal and local), trade journals, monographs, encyclopedias, interviews with trade associations and plant visits. In this part, the operating entities that were reported to be major small emission sources were studied in detail to determine the extent, type, and circumstances of the pollutant emitted from each. On the basis of this knowledge several evaluations were made. Industries were ranked according to total amount of pollutants emitted by each and again according to potential harm to environment of pollutants emitted by each. Determinations were also made regarding type of device (sorbent, catalytic incineration, or thermal incineration) which would be the most economical one to use to control the pollutant emission from each major operating entity. As primary objective of this phase of the study, recommendations are presented for future study to fill in the information gaps.

Part II, also entitled Package Sorption Device Technology Handbook, is the most important product of this study. In this part of the report several aspects of pollution control technology are considered, with the major emphasis, again, on the sorbent type systems. A theoretical basis is presented which permits the prediction of behavior of sorbents for the variety of pollutants emitted and circumstances of emission that would be encountered. Various sorbent systems are discussed with respect to their adaptability to air pollution control. Some systems are commercially available (activated carbon solvent recovery systems), some are proposed systems that have undergone limited pilot plant tests but have not as yet been reduced to commercial practice, and some are still in the conceptual stage, appearing sound on theoretical bases. Economic analyses are presented for the operation of carbon adsorbent systems, catalytic incinerators, and thermal incinerators under several operating circumstances. These results present a cost level that can be expected for pollution control and also indicate the operating conditions under which each of the three competing systems would be the most economical to use.

The appendix contains a bibliography pertinent to air pollution and its control by sorption and incineration.

Summary and Conclusions

Study Approach

To attain the objectives of the study, a procedure of action was devised to collect available information on: (1) small emission sources, (2) environmental effects of the emitted pollutants, and (3) packaged sorbent and catalytic incineration technology suitable for control of such sources. The collected information was analyzed and used to: (1) categorize the emission sources as to volume output and pollutant type, (2) evaluate the adverse environmental effects of pollutants from small emission sources and (3) evaluate the control technology in present use and further investigate the need and potential for development of new sorption system technology.

Information on emissions and control technology was sought from numerous sources: trade associations, local and state pollution control agencies, sorption device users and manufacturers, trade journals, text books, monographs, government documents, and vendor sales literature. The methods of data collection included plant visits to manufacturers and users of control systems. A questionnaire survey of pollution control agencies was also used to elicite information to identify and characterize small sources and their emissions.

Emission Sources Characteristics

Information Search

To fulfill the study objectives regarding emission sources in the most satisfactory manner, the study required detailed information on: (1) identity of small emission sources, (2) amount of pollutant emitted at each source, (3) concentration of pollutants in each emission gas stream, and (4) types of pollutants emitted in each gas stream. During the processing of data from the various information sources, it became apparent that emission data in the desired detail was not available. The questionnaire, which was sent on a trial basis to nine large pollution control districts, was expected to tap a rich source of detailed information of the required type. However, the response to the questionnaire was incomplete because of general lack of data of the type requested. The few agencies which do collect detailed emission data are not sufficiently staffed or funded to allow compilation of available data for the numerous requests they receive. The agencies in the State of California, in particular, have collected extensive data but would not provide it in any form other than formal reports and publications. Because of this problem, the study was of necessity developed from more approximate data as presented in the control district formal reports, trade association journals, and special reports. Information on types of pollutants were extracted from process descriptions as presented in text books, monographs and encyclopedias.

Extent of Small Sources Emissions

Based on survey figures given in formal reports from nine large air pollution control districts, - California South Coast Basin, San Francisco Bay Area, San Diego Bay Area, Delaware Valley, Denver, Hamilton County in Ohio, St. Louis, Washington (D.C.), and Jacksonville in Florida, - the estimated average rates of various types of gaseous emissions during the years 1968 to 1970 were:

Sources and type	Average rate, lb/da per 1000 people
All sources organic vapors (includes motor vehicle fuel and exhaust emissions)	800
Industrial processes organic vapors	100

The combined population of the survey areas was about 27 million, or over 13% of the total U.S. population. These are also the areas of greater population density; hence, the emission rates given are characteristic of areas where pollution problems are most acute and controls are most needed.

The 100 lb/da of industrial process organic vapors virtually comprise emissions from small emission sources. This rate, however, is not typical of all control districts; it is based on such widely varying rates as 20 lb/da for Denver to 156 lb/da for San Francisco Bay Area. To these rate figures should be added the emissions from an important small emission source, the petroleum distillate marketing chain, which did not appear in the industrial process emission rate figures. An average distillate emission rate for the nine districts could not be determined, but it is expected to be substantial because the average for the three California districts was 60 lb/da per 1000 people. Because of the variations in emission rates from area to area and lack of complete data for all areas, it was not possible to determine the proportion of emissions from small sources relative to organic vapors from all sources with exactness. The estimated portion is 15% with the balance being primarily from motor vehicles.

Small Emission Sources Identity and Ranking

Over fifty industries were considered in the study but for many of them comprehensive information permitting determination of their contribution to total organic emissions from small sources was lacking. The best guide in this respect was the California control districts which were the only ones to present any extensive breakdown of industrial processes into specific industries. On the basis of their data, 22 industries were identified as important small emission sources because of quantity of pollutants emitted or because of intense adverse effects of their pollutants on the environment. The emissions from them are predominantly organic except for the zinc plating operations which emit only NH_3 and HCl. Rubber products and domestic incineration also emit SO_2 and the rendering industries, H_2S.

Industry	Emission rate, (1) lb/da per 1000 people
Surface coating	96
Degreasing	20
Dry cleaning	10
Graphic arts	3
Plastic products	30
Rubber products	
Adhesives production	
Paper coating	
Vegetable oil extraction	
Organic liquid marketing and storage	
fuel	~60
nonfuel	5.1
Meat rendering	0.25
Fish rendering	
Canning	---
Food serving	1.6
Coffee roasting	0.02
Tobacco curing	---
Tanning	---
Meat smoke treatment	---
Domestic incineration	140
Zinc plating	---

Baking	0.04
Candy making	---

(1) For some industries (as for instance canning) no rate figures were given, but are recognized as pollutant emission sources of importance.

The industries comprising the small emission sources were classified into two groups: (1) the solvent user industries, the first ten in the list, and (2) the process industries, the last twelve in the list, which generate pollutants through thermal, chemical, or biological processes. The solvent user industries clearly emit a larger volume of pollutants (solvents) than the process industries, except for domestic incineration. Domestic incineration was permitted in the San Francisco Bay Area at the time of the survey, but the general trend in the country is to ban all domestic incineration, and dispose of solid refuse by means which do not pollute the atmosphere.

The surface coating industry, the largest solvent emitter, is comprised of many small operating units. Of these, the industrial spray booths are the most numerous and are responsible for 45% of the surface coating emissions. Emissions from ovens and dryers used to cure the coatings contribute 17% of the total. Nonindustrial means such as outdoor painting contribute 36%.

The next largest organic vapor emitting industry is the industry indicated as organic liquid marketing and storage. This includes, as the major entity, the petroleum distillate distribution and marketing chain where the largest vapor losses occur from gasoline marketing.

The other solvent user industries drop off considerably in emitted volumes.

Type of Pollutants

The chemical species of pollutants emitted from solvent user industries and process industries are quite different. Solvent emissions from the degreasing and dry cleaning industries are predominantly the chlorinated solvents, - trichloroethene, tetrachloroethene, trifluorotrichloroethane - the three most commonly used ones. Solvent emissions from other users are: hydrocarbons (aromatic, olefinic, naphthenic and aliphatic), alcohols, ketones, ethers, glycol ethers, esters, and nitroparaffines. In these industries the nature of the emission is quite predictable from the solvent blends entering the process except where high temperature drying or baking operations are carried out. In these cases the pollutant mixture may also contain decomposition products of drying oils, resins, and high boiling solvents.

Pollutant emissions from the process industries are predominantly decomposition products of materials entering the process. The chemical species found in the emissions from various thermal processes are predominantly aldehydes, organic acids, amines and sulfides.

Conditions of Pollution Emission

In addition to pollutant type, the conditions of pollution emission such as concentration, total gas flow, gas temperature, humidity, and particulate matter in the gas stream also vary between emission sources and must be known before the source can be characterized and the type and size of control system best suited for its control determined. Recovery value of the pollutant is an additional factor that has an important bearing on the selection of control system. To obtain the necessary information on operating conditions and determine the best suited control system, an in-depth study was done on each of the 22 industries as listed.

For pollutants of low recovery value, the favorable conditions for control by incineration are, high concentration and/or elevated temperature. Emissions from coffee roasting and meat smokehouses occur under these conditions. For pollutants of high recovery value, carbon adsorbent systems are highly economical to operate when the concentration is high and gas temperature is moderate. Emissions from most of the solvent user industries occur under these conditions.

Environmental Effects

Pollutants produce effects in the environment through various means that make life unpleasant or difficult. Most important is the toxic effect which can produce discomfort, illness and lower the performance efficiency of humans and animals. Pollutants can cause serious damage to vegetation. Other effects are damage to property through corrosion, discoloration and soiling. A nuisance effect which arouses the most immediate complaint is the bad odor response to many pollutants. Some pollutants, although not directly damaging to the environment, react with nitric oxides with the aid of the sun's radiation to produce smog which obscures visibility and produces discomfort and illness since it contains oxidants that are toxic.

The pollutants emitted by the solvent user industries are not highly toxic nor malodorous (except for H_2S from rubber products), but about 20% of them are smog precursors. Their damage to the environment is primarily by this route. Smog precursors have been identified with branched chain ketones, substituted aromatics and hydrocarbons containing unsaturated bonds. Aldehydes are also smog precursors but are rarely used as solvents. Los Angeles County Air Control District recognized this factor as a major cause of air pollution and issued Rule 66 which drastically limits the use of smog active solvents.

Compared to solvent emissions, the pollutant emissions from process industries are more toxic, malodorous and corrosive. The latter emissions also contain a large portion of aldehydes and olefinic compounds and thereby also contribute to smog formation. Because of the small quantity of pollutants emitted, the threat to the environment by the process industries is considerably less than that from the solvent user industries.

Packaged Air Pollution Control Devices

Information Sources

Most of the information that proved of value in this area was obtained from technical reports in scientific society and trade journals, from monographs, sales literature, and discussion with technical representatives of manufacturers of devices, catalysts and sorbents. Information was sought and found on theoretical aspects of adsorption and catalytic combustion, types of available devices, their potential applications to small emission sources, their operations and maintenance, and their operating costs.

Characteristics of Pollution Control Devices

Sorbents - The scope of this study included all types of sorbent systems that would be adaptable for air pollution control. There are three types of sorbents in use for various purposes; namely, chemisorbents, polar adsorbents, and non-polar adsorbents. Chemisorbents and polar adsorbents are not generally applicable to control of gaseous pollutants under the conditions of their release from small emission sources. Chemisorbents would have very limited application; they are highly selective since sorption is determined by highly reactive functional groups in the pollutant molecule. Polar adsorbents, of which silica gel, activated alumina, and molecular sieves are the best known examples, are effective for dehumidifying organic gases. Since pollutant-air mixtures invariably contain moisture, polar adsorbents, because of their affinity for moisture, would not be effective for pollution control for any practical length of time. The nonpolar activated carbons preferentially adsorb organic vapors, the type of vapors emitted from small emission sources. Further study thereby narrowed almost exclusively to sorption control devices using activated carbons.

Activated Carbon Adsorbent Systems - Activated carbon adsorbent systems, as presently manufactured for industrial and commercial uses, are oriented toward "air purification" and "solvent recovery". In either system the solvent or pollutant and air mixture is passed into the granular activated carbon bed wherein the adsorbable gas or vapor is retained by the carbon and the purified air passes through. When the carbon has reached its capacity to retain vapor, the gas mixture flow is stopped or diverted to a system containing fresh carbon.

Air Purification Systems - Air purification is carried out in a closed system, i.e., the carbon purified air is recirculated into the occupied space. Make-up air from outdoors is added to the recirculating airstream to maintain CO_2 and moisture concentrations at acceptable levels.

The carbon beds in air purification systems are thin; depths of 0.5 to 3.0 in. are in frequent use. Bed areas are sized to control airflow velocity in the 20 to 60 ft/min range with most operated at about 40 ft/min. Coarse mesh carbons of 4 to 6, 4 to 8 and 4 to 10 U.S. sieve number are used. The thin bed, the relatively low airflow velocity, and coarse mesh all contribute to low airflow resistances which are generally below 0.25 in. of H_2O pressure drop. The service times attained vary from 6 mo, when the odor concentration is described as heavy, to much longer periods of up to 2 yr, when odor concentration is described as light. These are nonregenerative systems, i.e., the carbon bed cannot be readily regenerated in place. At the end of the service time, the spent carbon beds are removed from the cells and the carbon is reactivated with high temperature steam at the carbon manufacturer's plant. In an atmosphere where the pollutant concentration is higher than 1.0 ppm, the frequency of carbon bed replacement would greatly increase and the operating costs would rise to prohibitive levels. When the concentration is 10 ppm or higher a regenerative type system becomes a definite economic necessity.

Although these systems have been intended for internal use, they are well suited for control of emission sources where pollutant concentrations are low but need to be controlled because of highly malodorous or toxic emissions.

Solvent Recovery Systems - In solvent recovery systems the spent carbon is regenerated within the system with low temperature (212°F) steam. The solvent is separated from the steam by condensation and decantation or distillation. Profitable solvent recovery is possible when the solvent is relatively high priced and vapor concentrations are high during the adsorption phase. Profit-loss breakeven concentration for most solvents is near 700 ppm, hence, the interest in the past has been on solvent vapor concentrations well above 700 ppm level.

Three types of solvent recovery systems are in use as differentiated by the manner in which the carbon bed is maintained or handled during the adsorption and regeneration phases of the operating cycle. These are:

Fixed bed
Moving bed
Fluidized bed

In the fixed bed system the carbon bed is usually contained in a vertical or horizontal tank with airflow usually downward through the bed. Bed areas are sized to control airflow velocity at near 100 ft/min. Bed depths vary from 12 to 36 in. A coarse mesh activated carbon, usually 4 to 6 U.S. sieve number, is used to maintain airflow resistance at a practical level. The pressure drop through the bed can vary from 6 to 18 in. of H_2O. Because the adsorptive capacity of carbon decreases with increase in temperature, high inlet air temperatures are avoided, temperatures below 130°F are recommended.

Other components of the solvent recovery system may include duct work, a particulate filter, inlet air cooler, blower, condenser for the solvent-steam mixture, decanter, distillation column, steam generator, and control instruments. The cyclic operations of the recovery system are very often automated with the various valves and other moving parts motor operated.

The fixed bed system is the least complicated of the systems available, has the least moving parts and is the most trouble free. It is also the largest in size per unit air handling capacity.

In the moving bed system, the carbon may be confined in a retainer and the retainer moved alternately between the part of the system where adsorption occurs and the part where regeneration occurs. In one system that employs this concept, the carbon is retained in the annular space between two perforated cylinders. As the cylinder or "rotary bed" is rotated, divided sections of the bed pass through an area where the vapor-laden air is directed radially inward through the bed to carry out the adsorption phase. Simultaneously at a different area of the rotary bed, previously spent sections of the bed are regenerated by low pressure steam directed outward through the bed. On each rotation, all sections of the rotary bed undergo an adsorption-regeneration cycle.

The advantages of the rotary bed system are: (1) the system is compact and (2) it utilizes shallower beds than the fixed bed system and thereby, for a given airflow capacity, is operated at a lower pressure drop. The disadvantages are associated with maintenance of the larger number of moving parts and seals that are necessary to separate the adsorption and regeneration sections of the system.

In fluidized bed systems, a high upward airflow velocity (240 ft/min) is maintained through the carbon bed which expands the bed and produces continuous movement or agitation of the carbon particles. In the fluidized bed adsorber, the carbon is caused to flow in a fairly thin layer (4.0 in. deep) across successively lower horizontal trays that are stacked vertically. The solvent laden air flows upward through the trays making contact with the carbon in a countercurrent manner. The spent carbon, withdrawn from the bottom tray, is elevated to an overhead tank in which the carbon is moved downward countercurrent to the flow of low pressure steam to desorb the solvent and regenerate the carbon for recycle through the system. The countercurrent contacting of the fluids and carbon in both phases of the adsorption-regeneration cycle offers a more efficient utilization of the carbon and regenerating steam. Large volumes of air can be stripped of vapors with a relatively small recovery system and consumption of steam is greatly reduced. An important disadvantage is the loss of carbon by attrition. This also produces carbon dust in the exhaust stream which should be filtered out to avoid air pollution.

The results of this study have shown that modifications to the present-type solvent recovery systems and changes in their operating procedures offer some of the more economical approaches to controlling pollutant emissions, specifically at concentrations below 700 ppm, down to the 1.0 ppm level where the air purification system becomes more economical to operate. To indicate the broader application for the (regenerative) solvent recovery type systems they are designated as carbon resorb systems in this report.

Carbon Resorb Systems - A controlling factor in the operation of carbon resorb systems at low concentrations is the small operating capacity and difficulty of regeneration. At decreased vapor concentrations the available operating capacity becomes smaller but the amount of regenerating agent required becomes larger. If steam is used, the amount required is so large that it is usually impractical to separate the vapor from the steam. By using air or inert gas at elevated temperatures for regeneration the desorbed-vapor disposal problem is alleviated. The desorbed vapor can now be incinerated, or readsorbed onto a secondary carbon bed and recovered by conventional steam regeneration or recovered by condensation. In each case the auxiliary device for the disposal operation is small and operable at low cost because of the high vapor concentration in the regenerating gas stream.

Incinerators or Afterburners - To place the effectiveness and economics of carbon resorb systems for pollution control in proper perspective, a limited evaluation of the competing systems, - catalytic and thermal incinerators, - was necessary.

Catalytic and thermal (direct-flame) incinerators are effectively used in many applications to control pollutant emissions where other means would be less economical. The use, however, becomes of questionable value when the pollutants contain halogenated, sulfonated, or nitrated hydrocarbons since these functional groups are converted to inorganic acids which may be more harmful than the pollutant in its original form.

The efficiency of each system increases as the operating temperature and gas residence time are increased. In practice 90% to 98% efficiencies have become acceptable performances because of various factors which limit the maximum temperature and residence time. For thermal incineration the generally used furnace temperature range is 1200° to 1500°F and for catalytic incineration it is 600° to 900°F. The residence time for both is generally between 0.05 and 0.5 sec.

The factors that are important in determining the merits of the incinerators relative to carbon resorb systems for pollution control are the cost of heating the air to the incineration temperature and the catalyst life. At concentrations below 100 ppm, the combustion of the pollutants contribute very little to heat input; the major portion of the heating load is borne by an auxiliary heater. As the combustible pollutant concentration increases the supplementary heating requirements decrease. At a specific concentration for each pollutant the combustion becomes self-sustaining. The pollutant emission streams often contain trace amounts of inorganic acids on particulates which can deactivate the catalyst, making necessary costly catalyst replacement.

Economic Analyses

Operating costs were estimated for carbon resorb, catalytic incineration and thermal incineration systems at pollutant vapor concentrations ranging from 10 to 7,000 ppm. The results of these analyses are presented graphically in Figure 6-31 which shows the cost of cleaning air in \$/hr per 1000 ft^3/min of airflow. At 10, 500 and 4,000 ppm pollutant concentration levels, the cleaning costs for the three types of control systems for an influent airstream at 77°F are:

	\$/hr per 1000 ft^3/min		
System	10 ppm	500 ppm	4,000 ppm
Carbon resorb	0.65	0.85	0.90
Catalytic incineration	0.95	0.85	0.60
Thermal incineration	1.27	1.10	0.70 to 0.95

As the vapor concentration rises above 500 ppm, more frequent regenerations are required and the operating cost of the carbon resorb systems rises. Unless the pollutant vapor has recovery value, the carbon resorb systems are not as economical to operate as the incinerators at these higher concentrations. At concentrations above 4,000 ppm air cleaning costs with carbon resorb systems increase to the \$0.90/hr per 1000 ft^3/min level while the costs with incinerators drop to \$0.60/hr per 1000 ft^3/min level and possibly lower.

At elevated airstream temperatures and low vapor concentrations the incinerators become increasingly more economical to operate and can approach the operating cost level of the carbon resorb systems.

Research and Development Recommendation

The results of the review and evaluation of existing, commercially available package devices for control of emissions from small sources show that for the areas of air purification (pollutant concentrations below about 1 ppm) and solvent recovery (recoverable solvent concentrations above 700 ppm) existing adsorbent system technology is generally adequate and the control devices are available. Significant short range benefits in emission reduction could be obtained by accelerated implementation of the existing adsorbent devices technology, particularly to the solvent user industries. The problem areas are in the process industries where research and development is required to demonstrate the effectiveness of carbon resorb systems.

The research and development plans recommend work in four areas: (1) emission and source characterization, (2) evaluation of new adsorbent systems, (3) generation of fundamental adsorption data, and (4) monitoring instrument development.

The objective of the emission and source characterization is to provide detailed chemical and engineering data necessary for the selection and design of optimally effective control systems. Evaluation of new adsorbent systems would involve laboratory feasibility studies on a potentially promising system and a final plant scale demonstration in one of the industries experiencing control problems. Adsorption-regeneration data useful to the design engineer of adsorbent systems is lacking; a program to generate this data would greatly expedite design work. To attain effective performance from many of the new proposed systems, monitoring and control instrumentation need to be developed.

Part I

Sources and Emissions, Environmental Effects, and Research and Development Recommendations

1. Sources and Emissions

Introduction

The systematic investigation of small pollutant sources and their emissions required the formulation of certain preliminary selection or screening criteria. The general guidelines provided at the outset of the program simply required investigation of all potential sources that could be amenable to control by packaged or off-the-shelf devices. The first and most important selection criterion was thus one of size or total emission volume. Analysis of the sizes of typical sorbent or catalytic oxidation devices placed an upper limit on total gas volume readily handled as being of the order of 10,000 scfm. In order to include air purification systems, where large volumes of air are handled for recirculation to working or inhabited areas, some consideration has been given to treatment of air volumes as large as 50,000 scfm. Above 50,000 scfm, sources are considered to be completely outside of the scope of the study.

As the study progressed and specific pollutant emissions were identified and related to the sources, additional criteria were developed and applied to the candidate sources. These criteria were based on the physical and chemical characteristics of the pollutants and on the operating parameter ranges for sorbent or catalytic oxidation systems. These criteria may be briefly summarized as follows:

Carbon Sorption Systems

(1) Molar volume (V_m) of pollutant in the range from 80 to 190 cm^3/mole.

(2) Pollutant concentration in the range from about 10 ppm to near 25 percent lower explosive limit (LEL).

(3) Exhaust stream either free of particulates or easily filtered.

(4) Exhaust stream moisture content controllable to below saturation, preferably below 80% RH.

(5) Exhaust stream temperature controllable to 130°F or below.

Catalytic Oxidation Systems

(1) Pollutant readily combustible.

(2) Pollutant concentration between 300 ppm and 25% LEL if gas temperature is near ambient.

(3) Pollutant concentration of less than 300 ppm if exhaust stream can be heated from 300° to 500°F.

(4) Exhaust stream either free of particulates or readily filtered.

(5) Exhaust stream free of catalytic poisons.

Thus, applying these criteria to a wide variety of potential emission sources resulted in the selection and classification of small emission sources suitable for more detailed study.

Information Sources

The major information sources utilized in the study included the trade magazines, technical literature, reports of related government contract studies, and data obtained by letter and interview contact with trade associations and pollution control agencies. To aid in the preliminary literature search, computerized key work abstract printouts were obtained from APTIC.

The trade associations and pollution control agencies contacted and reports of related government contract studies are listed in Appendix B.

At the outset of the program it was felt that a significant body of information pertinent to the study resided in the files of regional, state and municipal pollution control agencies. Many of these agencies have been involved in pollutant source inventory studies and control activities for years and thus should be a rich source of information.

A questionnaire was designed to elicit information from these agencies relevant to the identification and characterization of small sources and their emissions. The questionnaire, shown in Appendix B, consisted of two questions with a form for listing the desired information. The first question asked for a breakdown of the number of citizen complaints received per year by the agency with a check list of what were felt to be some of the more common sources with a cross listing of the type and nature of the complaint (i.e., odor type; effect on health, materials and vegetation, etc).

The second question asked for a listing of specific data on the sizes, rates and types of emissions and concentrations of contaminant species for each of the identified small source categories.

Preliminary contact was made with a number of control agencies to determine whether they had the type of information desired. Only nine agencies so indicated and thus were sent copies of the questionnaire. These nine were:

Area	Population (1969-1970)
San Francisco Bay Area, California	4,100,000
New York, New York	7,800,000
Houston, Texas	1,200,000
Jacksonville, Florida	510,000
Washington, D. C.	800,000
State of Illinois, Springfield, Illinois	11,000,000
Albuquerque, New Mexico	240,000
Pittsburgh, Pennsylvania	510,000
Vancouver, Washington	40,000
	26,200,000

Of these nine agencies which were sent questionnaires, six replies were received. Of these six, three agencies indicated that they could not supply the desired information for various reasons. These were San Francisco Bay Area, Houston and the State of Illinois.

The Washington, D. C. control office stated that they did not have sufficient information available to complete the questionnaire, but they did provide a record of complaints for 1970 grouped under the general headings of heating plants, incinerators, vehicles, open burning and miscellaneous. Leading the list of complaints, which totaled 1304, was the incinerator source category with 283.

Jacksonville and Albuquerque agencies completed the first question but were not able to supply relevant information for the second. The results of Question 1 are summarized in Table 1-I for the two areas. To permit combining of the numbers of the two areas, they are reported on the per million population basis.

Table 1-I **Number of Complaints per Year per Million Population**

	Sulfurous odor	Petroleum odor	Solvent odor	Food odor	Burning odor	Decay odor	Effect on vegetation	Corrosion	Ill-effect on health	Unidentified
Dry cleaning			20							
Paint shop			8		2					12
Print shop			4				2			
Gasoline transfer		2	2						2	
Restaurants				20	2					2
Food stores					160					
Small chem. mfg.	10		12					4		8
Incinerators				2	44			2		46
Woodwaste burners					80					
Sewage plants						80				
Pulp mills	4					8	2			10
Large chem. mfg.						20	4			2
Shipyards										36
Miscellaneous	2	10	10	10	6	20	8	2	2	228

No reply was received from the Pittsburgh-Allegheny County Air Pollution Control Office. However, on a prior visit to their office, data were obtained on complaints they had investigated. These were under headings such as smoke, open fires, coal deliveries, dust-fly ash, dumps, fumes-odors, and incinerators. The incinerator complaints for the first ten months of 1970 totaled 179.

The compilation of public complaints gives some indication of the types and frequency of noxious emissions, however, such data may be misleading. For example, a single source of annoyance may be the cause of all of the complaints within a municipality relating to that source category. The manner in which the complaint data are collected and compiled do not allow analysis of the number and distribution of individual sources which are the cause of complaint.

Certain source categories were identified by the survey which had not been previously considered. Significant among these are some large sources which, however, may have small unit operations amenable to control by packaged devices, such as wood waste burners, paper mill operaations and sewage disposal plants. Large chemical complexes are also often sufficiently fragmented as to be treated as a group of small sources.

After having contacted a number of local pollution control agencies, the original conception of the ready availability of relevant data from these sources was found to be incorrect. The most general response in the initial contacts, reinforced by the questionnaire returns, was a general lack of the type of data required. Additionally, those few agencies which have made any effort in this direction are not sufficiently staffed or funded to allow compilation of available data for the numerous requests which they receive. The agencies in the State of California in particular have collected extensive information but cannot provide data in any form other than their scheduled reports and publications.

Most of the activities of pollution control agencies have been directed toward definition and control of the major emission sources, with little attention thus far to those small sources which constitute only a small portion of the total pollutant emission load. Some relevant information was obtained from published regional inventories, however, because of the definition of certain small sources which when lumped together constitute a so-called major source. Examples of such small sources are the numerous individual solvent users (graphic arts, dry cleaning and surface coating establishments) which are generally lumped together as major sources in emission inventories. The detailed treatment of this type of data is presented in a later section of this chapter.

Emission Sources

Listing of Industries

Table 1-II lists 22 industries which, in part or in their entirety, are indentified as small, stationary, emission sources of vapor phase air pollutants. These industries were investigated to varying degrees of depth to determine the chemical nature of the pollutants, the amounts and concentrations of the emissions, and the operating conditions or circumstances of the emissions. This list is by no means complete, but includes those industries most frequently mentioned in surveys conducted in various air pollution control districts. The variety of industries represented gives a good indication of types of pollution problems which will be encountered for a considerable period of time in the future. Other existing and potential sources of emission are listed on page 1-67.

The list of industries in Table 1-II is divided into two groups on the basis of pollutant control methods. Those in the first group have processes amenable to control with activated carbon adsorption systems, although in some cases operated in conjunction with absorption and/or catalytic or thermal incineration systems.

Those in the second group are not amenable or are economically borderline in regard to pollutant control by the carbon adsorption systems. Catalytic and thermal incineration systems are more economical if the pollutant concentration is high, the emitted gas temperature is high or the pollutant mixtures contain low molecular weight pollutants not controllable by adsorption. In no case is the emitted pollutant of sufficient value to be recovered.

Categorizing of Industries

The first nine industries in the first group are solvent users wherein the solvent passes through the operations essentially unchanged and is ultimately released by one or more of

Table 1-II Small Stationary Emission Sources of Air Pollutants Grouped According to Preferred(1) Control Device, Estimated Emission Rates

Industry	Emission rate, lb/da per 1000 people exposed	Identification number
Preferred Control With Sorbent Devices		
Surface coating	96	1
Degreasing	20	2
Dry cleaning	10	3
Graphic arts	3	4
Plastics	30	5
Rubber products		6
Adhesives		7
Paper coatings		8
Vegetable oils		9
Organic storage evap.		
fuel	<60(2)	10
nonfuel	5.1	
Meat rendering	0.25	51
Fish rendering		52
Canning	---	53
Restaurants	1.6	54
Baking	0.04	58
Candy making		59
Preferred Control With Catalytic or Thermal Incineration		
Coffee roasting	0.02	55
Tobacco curing	---	57
Tanning	---	60
Meat smokehouses	---	61
Domestic incinerators	140	63
Zinc plating	---	65

(1) Based on economic analyses

(2) Rate based on the three California survey areas for petroleum fuel in 1968

several means. Because of the solvent volatilities, the major means of release is by vaporization while some may be retained by the product produced or retained in sludge or solid wastes produced by the operation. Unless some form of control is practiced, the evaporated portion becomes an atmospheric pollutant. Except in the case of industry start up or where incineration is used for pollution control, the amount of solvent sold per year to each industry is a measure of its pollutant emission rate. Some of the solvent users of combustible solvents, such as the surface coating and graphic arts, use incineration; hence, the solvent sales to them is an over estimated measure of their pollutant emission rates.

Industries listed with identification numbers 51 and larger are chemical or thermal processing industries. Pollutant vapors are emitted from them as an undesirable byproduct. In these cases direct measurements are required to determine the pollutant emission rates which, in many cases, have been difficult.

The identification numbers associated with the industries are used for reference purposes to identify the pollutant with the industry. Since the list does not include all the present (and also future) potential emission sources, the numbering system has been designed to allow future insertions into the two broad groups. Those from 1 to 50 inclusive are the solvent users and those numbered 51 and above are chemical, thermal, and biological process industries.

Extent of Emission

In order to: (1) determine the extent of pollutant emissions from small sources relative to the extent from all sources and (2) determine the amount of pollutants emitted by small sources for quantitative ranking, a review of published area emission inventories was conducted. Emission inventories were obtained of eight metropolitan areas, made by local or federal pollution control agencies. These inventories have reported, with varying degrees of precision, the total pollutant emissions from all sources as well as breakdowns by type and source category. The most complete and accurate inventory available is that published by the San Francisco Bay Area APCD. This inventory gives a rather detailed breakdown by major pollutant type and individual source category, including a number of categories identified as being of pertinence to this study.

Other inventories available were much less explicit in their reported emission estimates and, in general, are based on rapid emission estimating methods rather than actual surveys.

Table 1-III presents the estimated gaseous pollutant emission rates reduced to pounds per day per thousand persons (lb/da per 1000 people) for each of the reported area surveys. Column 2 gives the rates for all sources, stationary and mobile, and all types; i.e., oxides of sulfur and nitrogen, carbon monoxide and the rates for organic vapors from all sources, namely: petroleum refineries, chemical plants, incinerators, metallurgical plants, organic solvent users, power plants, agricultural burning and motor vehicles. Column 4 gives the emission rates of solvents and industrial organic vapors - those vapors that are of primary concern to control by the package sorbent systems. The extent of the latter, relative to pollution from all sources, is given as percentage in Column 5.

The combined population of the survey areas is about 27 million or over 13% of the total U.S. population. These are also the areas of greater population density; hence, the emission rates given are most characteristic of areas where pollution problems are most acute and controls are needed most.

Air pollution from all sources and all types is of the order of 5,000 lb/da per 1,000 people. About 3,500 lb, or 70%, of it is carbon monoxide, emitted mostly by motor vehicles. Organic vapors from all sources are emitted at a rate of the order of 800 lb/da per 1,000 people. In this case also, the emissions from motor vehicles constitute about 550 lb, or 70%, of the total organic emissions. Of the balance, 10% to 15% are emitted by the solvent users and the rest by the process industries including incineration and evaporation of organic liquids from storage or during transfer. The volume of emissions from the process industries is quite small except where domestic incinerators are in use, as in the San Francisco Bay Area (1969). The emission rate of small sources is of the order of 2% of the total emissions or, as stated above, about 10% to 15% of all organic vapors.

Of the various pollutant inventory surveys conducted throughout the country, the three California survey areas (first three in Table 1-III) identify the sources to a greater extent than the others. The emission rates as given in Table 1-II are from a 1969 San Francisco Bay Area survey, except for the organic storage evaporation. The Bay Area data are shown in greater detail in Table 1-IV.

Table 1-III Rates of Gaseous Pollutant Emissions From Nine Survey Areas, Pollutant Emission Rate, lb/da per 1000 People

Survey area	All types, all sources	Organics, all sources	Industrial process organics	%(3)	Reference
South Coast Basin	4,000	720	117	2.9	Cal. (1968)
San Francisco Bay Area	4,700	960	156	3.3	Cal. (1968)
San Diego Bay Area	3,700	630	65	1.8	Cal. (1968)
Delaware Valley	5,700	840	44(1)	---	Wohlers (1965)
Denver, Colorado	---	---	20	---	Dobler (1971)
Hamilton County, Ohio	3,900	480	45	1.2	Smith (1970)
St. Louis Study Area	6,400	740	96	1.5	McGraw (1968)
Washington, D.C. Region	---	680	6(2)	---	Maryland (1970)
Jacksonville, Florida	6,950	1,300	---	---	Sheehey (1963)
Averages	5,000	800	100	2	

(1) Surface coating and dry cleaning solvents only
(2) Dry cleaning solvents only
(3) Percentage of industrial process organics relative to all types

Table 1-IV Amounts of Organic Pollutants Emitted by Small Stationary Sources Based on San Francisco Bay Area (1969) Report

Industry	Number of operating units	Tons/day		Lb per day per 1,000 people		Lb per day per operating unit
Surface coating						
Spray booths	2,500	87.7		42.8		70
Ovens and dryers	750	34.1		16.6		91
Flowcoaters, dip tanks & washers	270	3.9		1.9		29
Brushing, rolling, nonindustrial spraying	---	72.0		35		
			197.7		96	
Degreasers	600		42.8		21	143
Dry cleaning						
Halogenated solvent	1,050	9.6		4.7		
Stoddard solvent		12.6		6.1		
			22.2		10.8	42
Graphic arts, printing	---		9.9		5	
Plastics, resin, putty mfg	---		29.4		14	
Surface coating, rubber products, pharmaceutical mfg	---		12.0		6	
Other solvent users, possibly adhesives, rubber products, paper coatings, extraction of vegetable oils	---		25.4		12	---
Total for solvent users			339.4		165	---

Table 1-IV (continued)

Industry	Number of operating units		Tons/day	Lb per day per 1,000 people	Lb per day per operating unit
Animal rendering	25		0.52	0.25	42
Fish rendering	---		----	----	---
Canning	---		----	----	---
Feed, fish oil & protein	---		----	----	---
Coffee roasting	78		0.04	0.02	1.0
Restaurants	15,000		3.19	1.6	0.4
Tobacco curing	---		----	----	---
Baking	---		0.08	0.04	---
Candy manufacture	---		----	----	---
Smoke houses	---		----	----	---
Tanning	---		----	----	---
Breweries & distilleries	---		----	----	---
Domestic incinerators	1,080,000		279	136	0.52
Conical incinerators	---		----	----	---
Sulfite pulp mills	---		----	----	---
Auto-refueling stations					
Underground tank	20,000	24.3			2.4
Auto-tank filling	50,000	37.3			1.5
			61.6	30	
Pipe coating	---		----	----	---
Asphalt blowing	15		0.1	0.05	13

Of all of the small emission sources, the surface coating industry emission rate is the largest. Fuel evaporation, primarily that of gasoline, is the second largest rate. In both cases the emissions come from many small operations; in the latter case it is the automobile filling stations. The surface coating industry is constituted of various sized operations, some of the major ones being the lacquer spray booths in small local shops, and varying in size to larger ones in the machinery manufacturing plants.

These and other significant small sources are discussed in detail in later sections of this chapter.

Types of Pollutants

Listing of Pollutants

The number of pollutants emitted from small stationary sources is expected to exceed 200. Table C-I, in Appendix C, lists 167 compounds that have been identified with the 22 industries listed in Table 1-II. The chemical formula, the molar volume, V_m, boiling point and lower explosive limit, LEL, are important properties to be considered in developing the subject of sorbent technology. In the last column of the table are the industry identification numbers.

Adsorptive Characteristics

The pollutants in Table C-I are listed in decreasing order of V_m, the molar volume at normal boiling point, calculated according to the method of Le Bas (1915), Appendix D. This order of listing gives a general ranking of the pollutants in decreasing order of adsorbabilities. The ranking applies more consistently to adsorbabilities on activated carbons than to the polar adsorbents: silica and alumina gels. Adsorption on the polar adsorbents is highly selective, being influenced by the polarity or polarizability of the molecule as induced by negative groups such as the halogens, hydroxy and double bonds. Small hydroxy compounds such as water, inorganic acids and salts are strongly adsorbed, preferentially to organic compounds of much larger molar volume. On activated carbons the compounds of larger V_m tend to displace those of smaller V_m, with certainty of displacement increasing as difference in V_m increases. The displacement is not always complete; some coexistance can occur. On polar adsorbents, the same preferential adsorption occurs in mixtures of nonpolar organic compounds. Theoretical aspects of adsorption are discussed in greater detail in Chapter 4.

Because of the nonselectivity of activated carbons, except that due to differences in V_m, and the low level of interference of water with organic vapor adsorption, activated carbons are used almost exclusively in pollutant vapor control when moisture is present in the exhaust gas stream.

On activated carbons, those pollutants with small V_m, listed in the lower end of Table C-I, become increasingly difficult to control with adsorption systems. Those with V_m larger than 80 cm^3/mol offer no real problem, at least, in the adsorption phase of the operating cycle, while those below are variable. Propane, propene, ammonia, methanol and methanoic acid require excessively large carbon beds or systems operation with very short adsorption-desorption cycle times to effect any pollutant control. Propanone, ethanoic acid, ethanol and dichloromethane are more amenable to control with practical sized carbon beds.

With regenerative carbon systems (also designated as carbon resorb systems), the ease or difficulty of pollutant desorption is also an important factor to be considered. Those in the upper end of Table C-I, with large V_m, are increasingly difficult to desorb with commonly used regenerating agents and at the relatively low temperatures commonly used. Regeneration with 212°F steam does not always effect complete desorption of compounds with V_m larger than 190 cm^3/mol, while those with smaller V_m are readily desorbed unless polymerization occurs. The accumulation of heavy or large V_m compounds will gradually deactivate the carbon over successive adsorption-desorption cycles, so that ultimately it will be necessary to discard the carbon or have it reactivated.

The V_m range in which the carbon resorb type system is most effective is from 80 to 190 cm^3/mol.

Identification With Industries

The number of pollutants that have been identified with each of the 22 industries investigated are given in Table 1-V. Not all possible pollutants from each of the sources have been identified, but the closest approach to complete identification exists in the surface coating, degreasing, dry cleaning and graphic arts industries which, as of 1969, were the major small stationary emission sources in regard to total emission quantity. The type of emissions from the other solvent users and also the meat rendering industry are well documented. For the other emission sources the important and predominant pollutants have been reported, i.e., those that will have a bearing on the type of control technology required.

Table 1-V Number of Pollutants Identified With Each Industry

	Number per industry			
		Number in V_m range		
Industry	Total	over 190	80 to 190	under 80
1. Surface coating	64	9	50	5
2. Degreasing	5		4	1
3. Dry cleaning	3		3	
4. Graphic arts	82	11	62	9
5. Plastics	17	3	11	3
6. Rubber products	23		18	5
7. Adhesives	38	1	28	8
8. Paper coating	11	2	9	
9. Vegetable oils ext.	3		3	
10. Organic storage evaporation	10		9	1
51. Meat rendering	43	2	28	13
52. Fish rendering	6		3	3
53. Canning	--			
54. Restaurants	--			
55. Coffee roasting	5		1	4
57. Tobacco curing	8		1	7
58. Baking	1			1
59. Candy making	--			
60. Tanning	2			2
61. Meat smokehouses	7		2	5
63. Domestic incineration	--			5
65. Zinc plating	1			1

The breakdown of the totals into V_m ranges presents the most important criterion for determining the feasibility of using a carbon system for pollution control. Most of the emitted solvents and the pollutants from the meat-rendering plants are in the 80 to 190 cm^3/mol V_m range; hence, they are amenable to control when adsorption and regeneration are the controlling factors. Some of the solvents from surface-coating and graphic-arts operations have V_m larger than 190 cm^3/mol and may not desorb completely during regeneration, while some have V_m smaller than 80 cm^3/mol and may not be sufficiently adsorbed to make a carbon adsorption system economically favorable when compared to competing systems. Pollutants from the thermal processing industries, such as the coffee roasting, tobacco curing and smokehouses, tend to be small molecules with V_m smaller than 80 cm^3/mol. A fair portion of those emitted from the meat rendering industries also falls into this V_m range. Further information on exact molecular species and the emission source operating conditions is required before a final decision can be made on type and also size of the control system.

The classes of compounds used and/or emitted by the various industries follow a pattern. The solvent users, except for the degreasing and dry cleaning industries, use the hydrocarbons (aromatic, naphthenic and aliphatic), alcohols, ketones, ethers, glycol ethers, esters and nitroparaffins. Classes of compounds appearing as pollutants from the thermal process industries are predominantly aldehydes, organic acids, amines and sulfides. Chlorinated solvents are predominantly used in the cleaning industries.

The most generally used nonhalogenated solvents are listed in Table 1-VI. In the surface coating and graphic-arts industries the solvents are used in blends of two to twelve to obtain the desired viscosity, solvency power, drying rate and compatibility with the drying oils and resins. Most frequently, the blends consist of two to four solvents. The two most frequently appearing solvents in the blends are toluene and xylene. All of these solvents are recoverable with carbon solvent recovery systems.

In the degreasing industry five halogenated hydrocarbons are used as listed in Table 1-VII. In 1967, about 90% of the tonnage of solvent sold for this purpose in Los Angeles County was trichloroethene and most of the remaining 10%, tetrachloroethene (Walsh, 1967). Most greases dissolve readily at 188°F in trichloroethene, hence its wide use. Tetrachloroethene is used when a higher temperature is required. For cleaning of electrical wire coils, motor components or other temperature-sensitive materials, the lower boiling solvents are used. Since the application of Rule 66, the use of trichloroethene has been restricted in Los Angeles County because of its smog forming properties and 1,1,1-trichloroethane is now the accepted solvent.

Table 1-VI Most Generally Used Nonhalogenated Solvents

Solvent	Vm, cm³/mol
Heptane	163
4-Methyl-2-pentanone	141
Hexane	140
Xylene	140
Toluene	118
Cyclohexanone	118
Ethyl acetate	106
Butanone	96
Benzene	95
Propanone	74
Ethanol	61

Table 1-VII Halogenated Solvents Used in Degreasing

Solvent	Vm, cm³/mol	Vapor temperature, °F
Trichloroethene	98	188
Tetrachloroethene	116	250
1,1,1-Trichloroethane	106	165
1,1,2-Trichloro-1,2,2-Trifluoroethane	120	118
Dichloromethane	65	104

In the dry cleaning industry two types of solvents are in use: the hydrocarbons and halogenated hydrocarbons. Those most frequently used are listed in Table 1-VIII. The trend of solvent usage is away from the Stoddard and 140°F solvents to the halogenated hydrocarbons, particularly the trichloro-trifluoroethane.

Evaporation of organic vapors from storage tanks and during transfer occurs in many industrial operations where volatile reactants or solvents are used. The largest emission rates occur in motor fuel storage and transfer.

The emission rate of 60 lb/da per 1,000 people, given in Table 1-II, is an average figure for motor fuels in the three California survey areas during 1968 (California, 1969). The list in Table 1-IX gives the mol fractions of the compounds in a typical gasoline vapor mixture.

Table 1-VIII Solvents Used in Dry Cleaning

Solvent	V_m, cm^3/mol	Boiling range, °F
Tetrachloroethene	116	250
Trichloroethene	98	188
1,1,2-Trichloro-1,2,2-trifluoroethane	120	118
Stoddard 45.7% paraffin 42.2% naphtha 12.1% aromatic	185 ave	349 to 410
140°F solvent 46.5% paraffin 41.9% naphtha 11.6% aromatic	185 ave	358 to 396

Table 1-IX Components of Gasoline Vapors

Organic compound	V_m, cm^3/mol	Mol %(1)	Boiling point, °F
Hexane	140	3.0	154
Pentane	118	2.0	97
2-Methyl butane	118	7.7	82
1-Pentene	111	5.1	Ca 84
Butane	96	17.4	31
2-Methyl propane	96	2.9	14
1-Butene	89	3.2	21
Propane	74	0.6	-48

(1) Balance air, 58.1 mol%

Of the gasoline fractions the propane will not be recoverable but it is present at a low concentration; hence, there will not be a significant economic loss.

In meat rendering operations, the pollutant vapors emitted are decomposition products of tallow or fats and proteins. About 43 compounds have been identified as listed in Table C-I, Industry No. 51, (IITRI, 1971). The aldehydes are the most frequent and most abundant class of compounds emitted, with organic acids, diols, amines, sulfides making up the balance. Some of the compounds appearing at the highest concentrations, 10% to 50% of the total pollutant-vapor mixtures, are as listed in Table 1-X.

Table 1-X Pollutants Appearing at Highest Concentration From Meat Rendering Operations

Pollutant vapor	V_m, cm^3/mol	Boiling point, °F
Hexanal	141	263
3-Methyl butanal	118	198
Butanoic acid	108	327
2-Methyl propenal	89	155
Propanoic acid	86	286

All of these vapors give bad odor responses, particularly the butanoic acid. Some of the amines and sulfides which are more offensive are emitted at lower concentrations. One of these is dipropyl sulfide.

Five very malodorous decomposition products have been identified with the fish rendering industry; these are listed in Table 1-XI with their odor detection thresholds (Conrad, 1971).

Table 1-XI Malodorous Pollutants Emitted From Fish Rendering

Pollutant vapor	V_m, cm^3/mol	Odor detection threshold, ppm
Dimethyl disulfide	103	0.0076
Trimethyl amine	92	0.0002
Ethanethiol	70	0.001
Propenal	67	0.210
Carbon disulfide	66	0.210

Pollutant vapor concentrations in exhaust air are low but, because of the very low odor detection threshold concentrations, the pollutant emissions create an odor problem.

Fish and meat canning and also meat preparation in restaurants emit some of the decomposition products of the rendering operations but of a considerably less malodorous nature.

The other processing industries - coffee roasting, tobacco curing, tanning, meat smokehouses and zinc plating - emit sufficient quantities of low-molecular-weight pollutant vapors to make overall control with sorption systems impractical. The reported pollutants for each industry are listed in Table 1-XII. Those for coffee roasting and meat smokehouses were reported as classes of compounds, but with each class consisting of some of the lowest molecular-weight members.

Conditions of Pollutant Release by Industry

In the preceding text, the general pattern of types and amounts of pollutants emitted by the various industries were examined. In order to select the most economical pollutant control system, it is necessary to have an understanding of the operating conditions under which each competing system is most effective and also to have detailed information on the operations of the emission source that affect or determine the type of pollutants and conditions of their release. Based on feasibility and economic studies, a number of generalizations have been worked up which establish the effect of pollutant release conditions on choice of control systems. These generalizations are discussed immediately following. Also, the more important pollutant producing industries have been investigated to varying depths to determine the circumstances of the pollutant emissions. These are also discussed under this section.

Effect on Choice of Control System

Thermal Incinerators - Thermal incineration would be used in preference to catalytic incineration, carbon resorb (regenerative) systems or absorption when:

1. The pollutant has no recovery value.
2. The pollutant is combustible and yields no new pollutants on combustion.

Table 1-XII Pollutant Vapors Emitted From Coffee Roasting, Tobacco Curing, Meat Smokehouses, Tanning and Zinc Plating Industries

Pollutant vapor	V_m, cm^3/mol
Coffee roasting	
Organics	140 for hexane
Phenols	105 for phenol
Mercaptans	55 methanethiol
Organic acids	42 methanoic acid
Aldehydes	30 methanal
Tobacco curing	
Asparagine	140
Ethanoic acid	64
Methanol	42
Methanal	30
Ammonia	22
Meat smokehouses	
Resins	
Ketones	74 for propanone
Phenols	105 for phenol
Organic acid	42 methanoic
Aldehydes	30 methanal
Tanning	
Methanal	30
Ammonia	22
Zinc plating	
Ammonia	22

3. The concentration is between 1,000 ppm and 25% of lower explosive limit. At this concentration range, the gas mixture can be at the 100°F level.

4. The concentration is below 700 ppm but gas-mixture temperature is relatively high, in the 500° to 700°F range.

5. The gas mixture contains vapors which would deactivate combustion catalysts.

6. The gas mixture contains considerable amounts of vapors of V_m larger than 190 cm^3/mol, which cannot be effectively desorbed from carbons, or that contain considerable amounts of vapors of V_m smaller than 80 cm^3/mol which are very poorly adsorbed by carbons.

7. The gas mixture contains completely combustible (to CO_2 and H_2O) particulates. Noncombustible particulates would have to be scrubbed or dry-filtered out.

8. The moisture content is very high.

Catalytic Incinerators - Catalytic incineration would be used in preference to the competing systems when:

1. The pollutant has no recovery value.

2. The pollutant is combustible and yields no new pollutant on combustion.

3. The concentration is between 300 ppm and 25% of the lower explosive limit. At this concentration range, the gas mixture can be at the 100°F level.

4. The concentration is below 300 ppm but the gas-mixture temperature is elevated - in the 300° to 500°F range.

5. The gas mixture does not contain vapors which would deactivate combustion catalysts.

6. The gas mixture contains considerable amounts of vapors of V_m larger than 190 cm^3/mol, which cannot be effectively desorbed from carbons, or contains considerable amounts of vapors of V_m smaller than 80 cm^3/mol, which are very poorly adsorbed by carbons.

7. The gas mixture contains no appreciable amount of particulates, or contains particulates which can be readily dry-filtered out.

8. The gas mixture is relatively dry.

Absorption Systems - Absorption systems using water spray would be used in preference to the other competing systems when:

1. The pollutant has no recovery value.

2. The pollutant is soluble in water.

3. The pollutant is poorly adsorbed on carbons; i.e., V_m less than 80 cm^3/mol.

4. The pollutant is biologically degradable.

5. The concentration is below 700 ppm if pollutant is combustible.

6. The gas mixture contains particulates that are difficult to dry-filter out.

Carbon Air Purification Systems* - Carbon air purification systems would be used in preference to the other competing systems when:

1. The pollutant has no recovery value.

2. The pollutant V_m is larger than 80 cm^3/mol.

3. The concentration is of the order of 1 ppm or less.

4. The gas mixture has no appreciable amount of particulates or has particulates that are readily filtered.

5. The gas mixture temperature is 130°F or lower.

6. Relative humidity of gas mixture is below saturation, preferably below 80%.

Carbon Resorb Systems* - With the carbon resorb systems, the limitations on their use depends to some extent on whether the pollutant has recovery value. When the pollutant has no recovery value, the resorb system would be used in preference to competing systems when:

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*See Chapter 6, pages 6-4 and -32 for discussion of these two systems.

1. The pollutant V_m range is 80 to 190 cm^3/mol.
2. The gas mixture has no appreciable amount of particulates or has particulates that are readily filtered.
3. The gas mixture temperature is 130°F or lower.
4. The relative humidity of the gas mixture is below saturation, preferably below 80%.
5. The pollutant concentration is in the range 10 to 700 ppm when pollutant is combustible and yields no new pollutants on combustion.
6. The pollutant concentration is 10 ppm or higher for noncombustible pollutants or up to 25% of lower explosive limit for pollutants that yield new pollutants on combustion.

When the pollutant has recovery value, Items 1 to 4 are the same as above. Restriction on concentrations are different than Items 5 and 6. For recoverable pollutants, the concentration is 10 ppm and higher for the noncombustible and up to 25% of lower explosive limit for the combustible.

Surface Coating Industry

The surface coating industry can be divided into two separate entities: those who manufacture the material and those who use the material. The manufacturing end of the business does not appear to be a principle concern to this study. Most companies are medium to large size with operations using closed cycle systems so that release of material to the air is extremely small. The exceptions to this generalization are the emissions from solvent storage and odors from varnish cookers. Of principal concern are emissions from the various users of the surface coatings.

Types of Surface Coatings - There are five main types of surface coatings: namely, paint, enamel, varnish, lacquer and shellac. Some of the differences are due more to modifications in formulation to mee[illegible] se requirements rather than to basic differences.

Paint is a highly pigmented drying oil, thinned with a low solvency power solvent, referred to as a thinner. The pigment can be a metallic oxide or a high molecular weight organic compound and is suspended in the vehicle. The drying oil is an unsaturated polymer which on exposure to air oxidizes and polymerizes further to form the resinous protective film. It is only partially soluble in the thinner. Mostly natural drying oils are used but the shift is toward the synthetic type. The formulation is directed to give a coating that protects the substrate from the weather and beautifies it, but tends to be low on abrasion resistance. Painted surfaces also tend to have a dull finish.

Enamels are basically the same as paints except that synthetic drying oils are used to a larger extent. The formulation is directed to give a coating of higher abrasion or wear resistance. Enamel coatings are generally glossy, smoother, hence easier to wash, but are harder or more brittle than paint coatings. Resistance to weathering tends to be lower.

Varnishes are colorless, or tinted with stain or small amounts of pigment, to maintain a high degree of transparency. The substrate beauty is enhanced by the coating. A synthetic drying oil is used, usually an aromatic modified tung oil, and thinned with a low solvency thinner both with higher solvency than those used in enamels. An almost complete solution of the drying oil occurs. The emphasis is on wear resistance and also weather and light resistance. The attempt here is to combine all the good qualities of paints and enamels and still have a tough resilient and transparent coating.

The above three coating materials after being applied to the surface, dry and cure by evaporation of the thinner and by an oxidation-polymerization of the drying oil to form the resinous film. In contrast to the above, lacquer and shellac vehicle consists of a resin dissolve in a high solvency power solvent. On application, the drying occurs by evaporation of the solvent and deposition of the resin-pigment film. The early lacquers consisted of a cellulose nitrate resin while the present ones are made with acrylic resins. Shellac resin is a natural occurring product synthesized in the skin glands of certain insects of India. Lacquer and shellac coatings have the disadvantage that the resin film will redissolve.

Methods of Application - There are five methods of application which are of possible interest to this study: namely, spraying, roller, dipping, flow coating, and tumbling. The most widely used methods are hand brushing and also hand roller application, but these are of limited interest since they are used in out door construction or maintenance jobs where the job site changes frequently, hence means of vapor collection are impractical. The other methods are used in applying industrial finishes, where continuous operation at a stationary site makes use of emission control devices feasible.

Each of the five types of coating materials can be applied by each of the six methods of application when appropriate modifications are made to the formulations, although some coatings are more readily applied by some methods than others. As an example, lacquer is best applied by spraying.

Each method is best suited for certain types of articles to be coated, as for instance dip coating for pipes, flow coating for automobile frames and bed springs, roller coating for flat sheets or panels, tumbling for small rounded objects such as buttons and spray coating for large uneven surfaces such as automobile bodies. For each application the coating viscosity and drying rate must be carefully controlled by the solvent or thinner formulation. For instance, in the dip and flow coating applications the coating should become fixed to a uniform thickness and not continue to drain toward the lowest point on the article after being coated.

An essential part of the applications is the drying-curing operation. The drying-curing operation may be with air at ambient temperature, or in ovens with forced heated air or radiant heat. Air drying occurs at temperatures below 100°F, hot air drying at 100° to 200°F and baking at 200° to 450°F.

Surface Coating Solvents - Little or no volatiles are expected to be released from the pigments, drying oils or resins during applications and during drying unless recommended drying temperatures are exceeded. Baking produces some odorous decomposition products. The vapor release is essentially the thinners and solvents used. Table 1-XIII contains a listing of some of the thinners and solvents which have been identified with the surface coating industry. The thinners are aliphatic hydrocarbons, turpentine, mineral spirits VM&P naphtha. They are mainly in paints, enamels and varnishes. The solvents are the aromatics, alcohols, ketones, ethers and esters. They are used to varying degrees in enamels and varnishes but mainly in lacquer and shellac. Table 1-XIVshows this breakdown of solvents used in surface coatings (data selected from Table 112 of Weiss, 1967). In enamels, varnishes and shellacs, the volatile portion is about 50% and in lacquers, about 77% by weight. In brush-on paints, the volatile content may be lower than 50%.

Table 1-XIII Estimated Air Pollutant Emission Rates, Surface Coating Solvents

Pollutant	Emission rate, lb per day per 1000 pop.
n-Decane	18
n-Nonane	
Stoddard	
n-Octane	
Turpentine	
Xylenes, o, p & m	17
Toluene	
n-Pentyl acetate	26
2-Ethoxyethyl acetate	
Ethyl acetate	
1-Butanol	
2-Butanone	
2-Methoxy ethanol	
1-Propanol	
2-Propanol	
2-Propanone	
Ethanol	

Table 1-XIV Surface-Coating Formulas on an As-Purchased Basis (Weiss 1967)

	Composition of coating, %					
Type coating	Nonvolatile portion	Hydrocarbons		Alcohol	Ketone	Ester & Ether
		Aliphatic	Aromatic			
Paint	44	56	--	--	--	--
Enamel	58	10	30	2	--	--
Varnish	50	45	5	--	--	--
Lacquer	23	7	30	9	22	9
Shellac	50	--	--	50	--	--

Many of the coatings are cured or baked at the higher temperatures (200° to 450°F) in which case the resins and other components can release small amounts of high molecular-weight vapors.

To show the general make-up of coating formulations with respect to solvent content, four have been selected from data given by Parker (1965) and are presented in Tables 1-XV, -XVI, -XVII and -XVIII. The first three - a primer, an enamel and a lacquer - are industrial finishes for appliances, machinery, metal furniture, automobiles, etc. The varnish formulation is for wood furniture, a manufacturing or repair-shop operation where solvent vapor control is possible.

Table 1-XV Gray Epoxy Appliance Primer Formulation

Material	Nonvolatile, %	Volatile, %
Rutile, titanium dioxide	8.0	
Lamp black	0.1	
Bisphenol A-epichlorhydrin epoxy resin	24.7	
Urea formaldehyde resin	18.7	
4-Methyl-2-pentanol		10.5
Butanone		12.1
Toluene		12.9
Xylene		13.0
Totals	51.5	48.5

The above primer is cured by baking 20 minutes at 385°F.

Table 1-XVI Acrylic-Epoxy Appliance Enamel Formulation

Material	Nonvolatile, %	Volatile, %
Rutile, titanium oxide	26.9	
Acryloid AT-52 (Rohm & Haas Company)		
50% acrylic resin	19.8	
12.5 cellulose acetate	4.9	
37.5% xylene		14.8
Epoxy resin		
50% bisphenol A type resin	13.2	
50% 2-ethoxyethyl acetate		13.2
Raybo 3 antisilking agent	0.1	
Xylene		5.3
2-Ethoxyethyl acetate		1.7
Totals	64.9	35.0

The above enamel is cured by baking for 30 minutes at 325°F.

Table 1-XVII Vinyl Lacquer Formulation for Aluminum Siding

Material	Nonvolatile, %	Volatile, %
Rutile, titanium dioxide	10.5	
Geon 427, vinyl resin	11.2	
Geon 433, vinyl resin	2.8	
Admex, epoxy polymer	1.4	
Thermolite, tin stabilizer	0.1	
4-Methyl-2-pentanone		24.6
Xylene		24.6
Solvesso 100		24.6
Totals	26.0	73.8

Solvesso 100 is 94% aromatic with probable boiling range from 317° to 350°F.

Table 1-XVIII Base for Furniture Rubbing or Flat Varnish

Material	Nonvolatile, %	Volatile, %
Modified phenolic resin	30.8	
Z 2 dehydrated castor oil	6.1	
Liquid oiticia oil	13.9	
Mineral spirits		49.2
Totals	50.8	49.2

The nonvolatiles of the varnish base are cooked at 510° and 460°F before being diluted to 50% solids with mineral spirits. Mineral spirits generally designate the predominantly paraffinic and naphthenic solvents of C_{10} to C_{12} range with boiling points from 300° to 400°F. To produce a rubbing varnish from the base, it is blended with VMP naphtha, aromatic naphtha, lead naphthanate, cobalt naphthanate and an antiskinning agent, yielding a final product that is 57% volatiles. VMP naphtha solvents (varnish makers and painters) are C_8 to C_{10} aliphatics, and the aromatic naphthas are in the same high boiling ranges as the mineral spirits.

The primer and enamel may be applied to appliances by dipping or flow-coating. To reduce the enamel to spray viscosity it is diluted further with xylene and 2-ethoxyethyl acetate.

Pollutant Emission from Surface Coating Industry - The combined information of Tables 1-II, -IV and -XIV allow quantitative estimating on the various types of compounds being emitted. In Table 1-IV, the brushing, rolling, and nonindustrial spraying methods appear to apply to outdoor applications and the emissions are therefore not controllable. This reduces the emission rate, of concern to this study, from 96 to 61 lb per da per 1000 population. Of the 61 lb, 43 lb are emitted from spray booths which use mostly lacquers and some enamels. The 43 lb/da per 1000 population is then a rough estimate of the emission rate of the aromatic, alcohol, etc type solvents. Of these solvents, the aromatics constitute about 40% of the total as based on the percentage figures given in Table 1-XIV for lacquers and enamels and also on a number of industrial finish formulations described in Principles of Surface Coating Technology (Parker, 1965). On the basis of these considerations the emission rates as given in Table 1-XIII were estimated.

Solvent Emission Control - As of 1969, the surface-coating industry in the California survey areas emitted the largest quantity of solvents into the atmosphere. The rates of emissions from the various surface coating operations as reported by the 1969 San Francisco Bay Area survey are given in Table 1-XIX.

Table 1-XIX Solvent Emissions from Surface Coatings Operations (Bay Area, 1969)

Type of operation	Number of operating units	Lb/da per 1000 people	Lb/da per operating unit
Spraying	2,500	42.8	70
Drying	750	16.6	91
Flow-coating Dipping Washing	270	1.9	29
Brushing Rolling Nonindustrial spraying	---	35	--
Total		96.3	

About one half of total emission volume comes from many spray booths, with an average rate of 70 lb/da per operating unit. These are various shops such as auto body repair shops and production line spray booths for industrial machinery and home appliances. Part of the drying oven emissions are from the lacquer coated products and part from enamel coated products as received from the flow coating, dipping and roller coating operations, the 35 lb/da emissions from brushing and nonindustrial spraying are not controllable by adsorption, leaving 61 lb/da of the total 96 lb/da as possibly controllable.

The survey of the literature and of the control equipment manufacturers has not brought out evidence of any widespread use of control devices in the surface coating industry. Carbon sorbent systems do not appear to be in use for solvent recovery purposes. Under the prevailing operating procedures, solvent recovery is not profitable. Where bad odors are emitted, as from baking ovens, a limited use of catalytic and thermal incinerators is reported. The reasons for lack of use of carbon solvent recovery systems vary with type of surface coating operation.

Spray booths are operated with face velocities of 100 ft/min and over as required by varied state laws. Spray booths of sizes to fall within the scope of small emission sources are commercially available. Booths of front opening area from 13 to 100 ft^2 and operated at 100 to 180 ft/min air face velocity are described in sales literature (Paasche, 1971 and Spray, 1971). Because of over spray of the articles being coated, particulates consisting of the pigments, drying oils and resins are released into the exhaust airflow. To avoid air pollution by a lacquer or enamel mist, either dry filters or water sprays are used to separate out the mist.

For effective use of a carbon resorb system, the spray coating particulates and water mist should be completely removed from the exhaust air. This is not always accomplished. The 100 ft/min and over air velocities tend to keep the solvent concentration low, below the approximate 700 ppm economic break even point. The use of mixed solvents reduces the carbon adsorptive to some extent; i.e., a single organic compound at a given concentration requires less carbon than a mixture of several with the same combined concentration. Recovery of a solvent mixture from the steam condensate, after regeneration, is more involved and hence more costly than a single-compound solvent.

To determine the nature of air pollution control from a spray booth using a carbon resorb system, estimates were made of unit size, total airflow, and cost of regenerating steam, when total solvent emission rate is 70 lb per 8 hr da and concentrations are 10, 100, 1,000 and 4,800 ppm. The calculations were made for an acrylic lacquer thinner of composition given in Table 1-XX.

Table 1-XX Composition of a Common Lacquer Thinner

Organic compound	Weight, %	Conc of each at 4,800 ppm total	
		ppm	vol,%
2-Ethoxyethyl acetate	17	480	10.0
Toluene	43	1,740	36.3
Propanone	40	2,570	53.7

The 4,800 ppm is 25% LEL for the mixture calculated with an equation based on Le Chatelier's modification of the mixture law (Le Chatelier, 1891). The equation is given in Appendix D.

Because of pressure drop and other considerations, the linear velocity through carbon resorb system beds is varied from about 20 to 110 ft/min. The minimum face velocity for spray booths is 100 ft/min; hence the area of the carbon bed must be sized equal to, or larger than, the spray booth front opening for a given total airflow. The results of the calculations are given in Table 1-XXI when the airflow is kept at the 110 ft/min maximum which then gives the minimum carbon bed area. The 110 ft/min velocity for the spray booth gives the maximum front opening area. Eight one-hour cycles are assumed to recover the 70 lb/da solvent emitted.

Table 1-XXI Carbon-Resorb System Size, Operating Conditions, Regenerating Steam Cost for Control of Spray-Booth Solvent Emission

C_i(1),ppm	F, ft^3/min	A,ft^2	W, lb	Δp in.H_2O	Cost of 212°F steam	
					$/lb solvent	$/da
4,800	150	1.3	97	25.6	0.03	2
1,000	700	6.4	194	10.8	0.08	6
100	7,000	63.6	800	4.5	0.24	17
10	70,000	636	3,000-5,700	3.1	1.20	84

(1) See glossary for definitions of terms

The results of Table 1-XXI show that at 4,800 ppm the steam cost is low enough (3¢/lb of recovered solvent) so that the overall recovery operation is profitable, since the approximate price of the solvent mixture is 10¢/lb. At 1,000 ppm the recovery would not be profitable, but would defray air pollution control costs. The economic breakeven point is at a concentration between 1,000 and 4,800 ppm. At the 100 and 10 ppm level, it would not be economical to distill any water soluble portion, in this case the propanone, from the large volume of steam condensate. At these concentrations, the more economical approach may be to regenerate the carbon with a hot inert gas or air and burn the solvents immediately.

Emissions from drying, if at baking temperatures, can and often do contain high molecular weight drying oil or resin breakdown products. Since these cannot be desorbed by steam, the cost of frequent change of carbon beds makes the recovery unprofitable but not necessarily less economical than the competing incineration methods as a pollution control.

When no high molecular weight resinous products are present in the emission gases - as in the case with flow coating, dipping, roller coating applications and also some oven drying operations - the desired goal to attain profitable recovery is to minimize air or ventilating gas flow to raise solvent concentrations up to the 25% LEL. It is also desirable to maintain airflows in or over the applications operations at a minimum to avoid premature drying oil oxidation and thereby change flow characteristics of the enamel.

Degreasing Industry

Description of Industries - Degreasing is a necessary step in the preparation of metal fabricated articles for surface coating, electroplating or other finishing operations. The cleaning operation is done in a packaged unit, termed the degreaser, which utilizes an organic solvent as cleaning medium, Table 1-VII. Depending on the complexity of the unit, the soiled article may be contacted by immersion in the hot solvent, by a warm rinse, by liquid spray and condensate. A high degree of cleanliness of the articles is attained by suspending the (cool) article in the solvent vapor. By condensation of the vapor the grease, oil or other soil is dissolved and washed down into the liquid phase (Kearney, 1960).

The basic vapor degreaser consists of a vapor generating sump containing the solvent and heater, a vapor zone above the sump and freeboard. A narrow water-cooled jacket around the upper part of the degreaser sets the maximum height of the vapor zone. Soiled articles are lowered into the vapor zone through the open top and freeboard and withdrawn by the same route when cleaned. Vapor condensate cleaning stops when the article temperature rises to the vapor temperature. The spray step aids in the cleaning of irregularly shaped articles or articles otherwise difficult to clean and is done while the article is submerged in the vapor zone. The essential features of the degreaser are illustrated in Figure 1-1.

Size of Degreasing Industry - San Francisco Bay Area (1969) reported, (Table 1-IV), 600 degreasers in operation with average emission rate of 143 lb of solvent per day per operating unit. The amount emitted per day averaged 21 lb per 1000 people. The latter average would apply more to industrialized areas and not give a good indication of national average.

Table 8 of ASTM STP 310 Report lists typical applications of vapor degreasing. The production rates give an indication of size of degreasing units used in industry. For degreasing by vapor-spray-vapor system, the smallest rate reported is 600 lb/hr of steel spark plugs to remove machining oil, and the largest is 40,000 lb/hr of steel automatic transmission parts to remove machining oil, chips and shop dirt. For degreasing by the warm liquid-vapor system, the smallest rate reported is 500 lb/hr of magnesium aircraft castings to remove polyester resins, and the largest is 12,500 lb/hr of aluminum tubing to remove drawing lubricants. For degreasing by the boiling liquid, warm liquid and vapor system, the smallest is 50 lb/hr of gold and tin

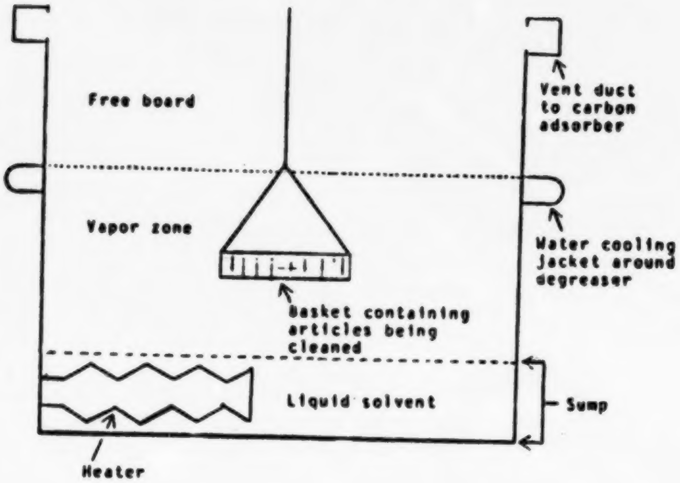

Free board
Vent duct to carbon adsorber
Vapor zone
Water cooling jacket around degreaser
Basket containing articles being cleaned
Liquid solvent
Sump
Heater

Figure 1-1 Degreaser Using Halogenated Hydrocarbon Vapors

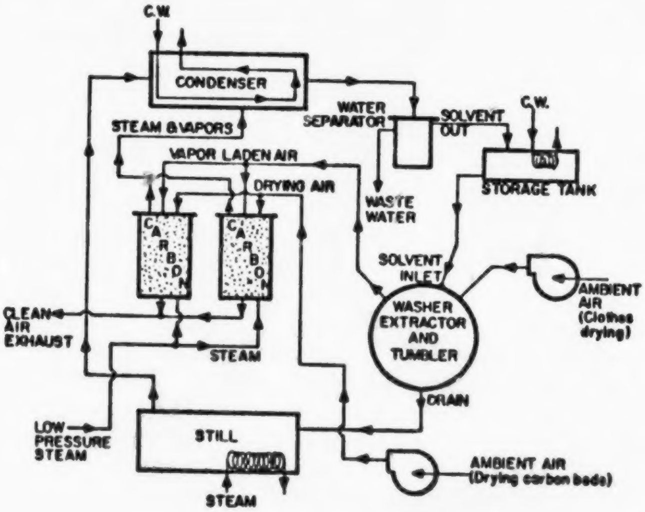


Figure 1-2 Dry Cleaning Machine With Integrated Carbon Solvent Recovery System. Courtesy of Vic Manufacturing Company

plated transistors to remove silicone and light oil, and the largest is 5,000 lb/hr of steel stampings to remove chips and light oil. Most of the materials handling is by conveyor and some by hoists. In the small operations, such as the transistor cleaning, the articles are lowered into the degreaser manually in wire mesh baskets.

Air Pollution from Degreasers - Solvents escape from degreasers under several circumstances. Degreasers must of necessity be operated with the top open completely, or partially open, or opened at intervals. Most of the vapors escaped by this route. Water-cooled condensers or jackets operated at 68°F can hold the vapor concentration at the vapor-zone-freeboard boundry to approximately the following concentrations for three of the most commonly used solvents.

Solvent	Concentration	
	Volume, %	ppm
Tetrachloroethene	1.9	19,000
Trichloroethene	7.9	79,000
1,1,1 Trichloroethane	13	130,000

In a very still freeboard atmosphere, a concentration gradient can form with very slow diffusion of vapors out of the degreaser. Vapor movement through the freeboard is greatly accelerated by air currents passing over an open or partially open degreaser, by opening and closing of the lid if one is used, and by the movement of the articles in and out of the degreaser. Movements necessary during spray cleaning create turbulences which accelerate vapor escape. Degreaser manufacturers estimate 0.05 lb/hr per ft^2 of open tank area as the vapor escape rate. Another potential means of vapor escape is by way of liquid solvent adhering to the articles being transferred out. This happens when the articles have not reached the vapor temperature. Also, pockets and crevices in the articles can carry out solvent. By careful operating procedures vapor losses can be minimized.

For a degreaser cleaning 40,000 lb/hr of transmission parts, the solvent distillation rate is 600 gal/hr and solvent make-up rate is 2.4 gal/hr (Kearney, 1960). Assuming trichloroethene, the total make-up or potential pollutant emission rate is 233 lb per 8 hr day. The mean calculated emission rate from San Francisco data is 143 lb per degreaser per day. Possible reasons for the difference can be that the average degreaser of San Francisco Bay Area would be smaller than the 40,000 lb/hr unit and some of the San Francisco degreasers have solvent recovery systems.

If it is assumed that a trichloroethene vapor is drawn off the (largest) 40,000 lb/hr degreaser at a concentration of 1,000 ppm, the airflow would be 1,450 ft³/min. The calculation is:

$$\frac{1{,}000 \text{ ppm} \times 10^{-6} \times 131 \text{ lb mol wt}}{391 \text{ ft}^3 \text{ mol vol}} F = \frac{2.4 \text{ gal/hr} \times 12.7 \text{ lb/gal}}{60 \text{ min/hr}}$$

$$F = 1{,}450 \text{ ft}^3\text{/min.}$$

The solvent can be profitably recovered under these conditions by several of the package solvent recovery systems on the market. Much of the solvent recovery system advertising is directed toward recovery of trichloroethene.

Emission Control - To control air pollution by way of a carbon solvent recovery system, slotted ducts are attached to the top rim of the degreaser as shown in Figure 1-1. The airflow through the slots can be optimized to: (1) minimize or avoid creating turbulence in the freeboard, (2) prevent or minimize escape of solvents past the slotted ducts, and (3) maintain solvent concentration in airstreams above 700 ppm, the approximate economic breakeven point.

This has been accomplished in a considerable number of installations. A case in point is a recovery operation reported by Berg (1968) in which 7,300 lb/wk (183 lb/hr) of trichloroethene were recovered with a carbon solvent-recovery system at 3,000 ft³/min airflow. The calculated concentration was 3,000 ppm. The recovery cost was 0.34¢/lb of solvent. It included electricity for controls and exhausters, steam, cooling water, and labor to clean filter bags ahead of the carbon beds each day. A comparison between operating cost and solvent selling price (11.5¢/lb) indicates a profitable operation.

The 2.4 gal/hr (29 lb/hr) solvent make-up rate reported above for one of the larger degreasers can be readily controlled by solvent recovery systems of less than 3,000 ft³/min air-handling capacity. The use of carbon resorb systems in the degreasing industry represents one of the more straightforward and trouble-free applications. For all practical purposes, the logical solution to pollution control in the industry is the installation of more recovery systems.

Dry Cleaning Industry

Description of Operation - The procedure consists of charging a weighed amount of clothing into the dry cleaning unit, washing by agitation in a solvent bath and rinsing with clean solvent. On completion of the washing step, the solvent is drained off and the liquid solvent in the clothing is removed by spinning in a centrifuge, termed the extractor. In the third and final step, the clothing is dried by means of heating air circulated through a tumbler. The solvent from the washer is reclaimed for reuse by filtration and distillation. Table 1-VIII lists the most used solvents.

Size of Dry Cleaning Industry - The dry cleaning industry of the United States is comprised of some 35,000 individual operations ranging from the small - grossing less than $40,000 per year - to large complex operations grossing over $300,000 per year. At present approximately 75% of the plants utilize tetrachloroethene. These tend to be the smaller operations and account for only 55% of the volume of clothes cleaned (National Drycleaners Institute interview). In Los Angeles County (1956), because of fire laws, the newer smaller commercial and coin operated dry cleaning establishments, which are generally near residential and shopping areas, use the chlorinated solvents. The larger dry cleaning establishments in industrial and commercial areas use the petroleum solvents (Lunche, 1957). About 60% (1957) use chlorinated hydrocarbons.

The Dry Cleaners' Association estimates that an average per day load of clothing for small operations, which are the majority of installations, would be approximately 400 lb. They further feel that there are few operations doing in excess of 800 lb per day. Based on tetrachloroethene vapor-recovery figures for Los Angeles County, the estimated daily clothing load for the average size tetrachloroethene plant is 570 lb.

Based on the 35,000 dry cleaners figure, the number of dry cleaners per 1000 people in the United States is 0.17. For the San Francisco Bay Area the estimate for 1969 is 0.26.

Air Pollution From Dry Cleaning - The San Francisco Bay Area survey (1969) on 1,050 dry cleaning units gave estimates on the amount of emitted chlorinated solvents at 4.7 lb/da per 1,000 people. The combined amount emitted per operating unit was estimated at 42 lb/da.

Solvent can escape into the atmosphere under several circumstances. In the older dry cleaning plants, the washer-extractor and tumbler (or dryer) are two separate operating components. When clothes are transferred from one to the other, solvent vapor is released into the atmosphere. Vapor released during the tumbler step is passed through a water-cooled condenser which removes part of the vapors in the airstream.

A survey of 60 (of 600) tetrachloroethene-type dry cleaners in Los Angeles County, 1962, showed that per 1,000 lb of clothing cleaning, 10 gal of tetrachloroethene are required when no carbon adsorbent recovery unit is employed. When an adsorbent unit is employed, the solvent loss is 3.5 gal or a recovery of 6.5 gal (88 lb). A 1971 estimate, by the National Dry Cleaners Institute, for tetrachloroethene recovery for coin operated machines is much smaller. For a 2,000-load cycle of approximately 17,500 lb of clothing, the recovered quantity was 25 gal or approximately 1.5 gal per 1,000 lb of clothing.

Emission Control - When a carbon solvent recovery system is used, it is installed at the discharge of the ventilating system to collect the vapor laden air from the tumbler and vents placed near the doors of the washer-extractor, the tumbler, and the floor near the tumbler. The floor vent collects solvent released from the clothing when removed from the tumbler.

In the construction of new dry cleaning machinery the trend is toward a completely contained machine which includes an activated carbon solvent recovery system. A flow diagram of this type of machine is shown in Figure 1-2. In a 14-min cycle time, the coin operated machine of this make cleans 8 lb of clothing; and a commercial unit, 25 lb. One gallon of 1,1,2-trichloro-1,2,2-trifluoroethane is used per pound of clothing in the wash phase of the overall cycle. Very little solvent is lost to the atmosphere.

The effective use of carbon resorb type solvent recovery systems has been demonstrated in the dry cleaning plants where halogenated solvents are used. Because of the high cost of tetrachloroethene, the value of its recovery makes possible the amortization of the adsorption unit within 1 to 2 yr; hence a financial incentive exists for the prevention of air pollution with the chlorinated solvents. Approximately 50% of these plants have activated carbon recovery units. Plants employing the petroleum type solvents, however, make no attempt at vapor recovery, at least in the United States, because of the lower cost of these solvents.

Graphic Arts Industry

Size of Industry - This multifaceted industry is pertinent as an emission source because of solvents or oils contained in the printing inks. The industry is composed of 40,000 establishments (U.S. Department of Commerce, 1970) of which close to 90% employ fewer than 20 persons. However, about one-half of the dollar volume of business is realized by the much smaller number of large establishments.

The printing activity is concentrated in urban areas, although distributed throughout the country. About one-half of all commercial printing is done in four states: New York, Illinois, Pennsylvania and California (Gadomski, 1970).

Printing Processes - The individual printing processes which comprise the graphic arts industry include letterpress, lithographic, gravure and screen process.

In the letterpress process, the printing area of the printing plate or roller is raised above the nonprinting area. Ink applied to the raised area is subsequently transferred to the paper or other substrate to be printed. Books, newspapers and magazines are printed by this process (Bruno, 1968).

In lithography, the image and nonimage areas are on the same plane. The image area is grease receptive and water repellent, while the nonimage area is the reverse. The ink applied to the image area is transferred to the substrate to be printed. General commercial literature, books, catalogs, greeting cards, letterhead business forms, checks, art reproductions and labels are printed by this process.

In the gravure process, the printing area is recessed; it is comprised of wells etched to different depths. The ink is transferred to the roller surface and excess removed with a blade. Longrun magazines, newspaper supplements, preprints for newspapers and plastic laminates are printed by this process.

In the screen process, a stencil is applied to a silk or stainless-steel screen to which a thickened paste ink is added. The ink is transferred to the printing surface by rolling with a squeegee. This process finds application in printing displays, posters and signs.

When the image is transferred directly from the image carrier to the paper, it is known as direct printing. When the image is transferred by an intermediate roller or plate, it is known as offset printing. All screen process and most letterpress and gravure processes are direct printing. Most lithographic printing is offset.

When the plates or rollers used in the letterpress process are of rubber, the process is known as flexography. This process is used widely in multicolor printing on a wide variety of substrates.

Printing Inks - The three important properties of inks are drying, printability and color. Of greatest concern to air pollution is the drying properties of the ink which can occur by one or more of seven different physical or chemical mechanisms; i.e., absorption, solvent evaporation, resin precipitation, oxidation, polymerization, cold setting and gelation. The choice of ink is determined by the printing process and the substrate to be printed, and the ink composition, in turn, determines the air pollution potential of the printing process.

Inks used in letterpress and lithographic processes are referred to as oil inks or paste inks. Most of these inks dry by means other than solvent evaporation, and those few that depend to a minor extent on solvent evaporation use solvents in 250° to 350°F boiling range. Liquid body is imparted to the ink to some extent by liquid reactants such as linseed oil. The solvents used are mineral oil, high boiling hydrocarbons in the 400° to 530°F boiling range and triethylene glycols.

Letterpress and lithographic newsprint inks contain aliphatic hydrocarbon solvents of 425° to 530°F boiling range. Initial or immediate drying after ink application occurs by absorption into the paper, with drying completed in heated ovens. Inks used on folding cartons and Kraftliner containers dry by oxidation and some inks, used in the latter, dry by precipitation. Metal-container inks dry by curing for 10 min at 300° to 400°F. Polymerization, oxidation, and crosslinking occur.

Inks used in flexographic and gravure processes are referred to as solvent inks and differ from those used in letterpress and lithography in that they are of very low viscosity and almost always dry by evaporation of highly volatile solvents. Those identified with the graphic arts industry in Table C-I are primarily those used by the flexography and gravure processes. However, because of the use of rubber plates and rollers, certain ones of these solvents cannot be used in the flexographic process. Toluene and xylene cannot be used at all; ketones can be used with butyl rubber, while hydrocarbons can be used with buna rubber. Alcohols, glycols and low concentrations (25%) of esters are acceptable. The boiling range of the solvents extends from 147° for methanol to 343°F for 2-butoxy ethanol.

Air Pollution From Graphic Arts - Without pollution control, volatile solvents are emitted into the atmosphere from the flexographic and gravure printing operations during the ink application and also during subsequent drying. As listed in Table C-I, 83 organic solvents have been identified with these two printing processes. The emission rate, essentially of these solvents, is estimated at 5 lb/da per 1000 people based on the San Francisco survey. Pollution from the letterpress and lithographic printing operations will differ considerably. Very little vapor emission will occur during the ink applications but, where high temperature oven drying is carried out, high boiling solvents will be emitted accompanied by some decomposition products of the drying oils and resins. The high boiling solvents emitted have V_m values considerably in excess of 190 cm^3/mol and would make carbon resorb or regenerative systems impractical for solvent recovery. The decomposition products add to the regenerative problem.

Emission Control - The extent of emission control in the various printing plant operations has been investigated by Gadomski (1970) through visits to 57 plants distributed in 10 states, namely: California, Illinois, Wisconsin, Georgia, Tennessee, Florida, New York, New Jersey, Pennsylvania and Ohio. Of the 57 plants, 40 plants use no solvent emission control devices. Of the remaining 17 plants 5 different types of devices or methods are used to control emissions. One plant, involved in metal decorating operations, uses a deodorizer unit wherein a deodorizing vapor is fed into the exhaust airstream. Another plant, also in metal decorating operations, uses a spray chamber. Seven plants involved in metal decorating and lithographic operations use direct flame afterburners, with and without heat recovery. Six plants, also in metal decorating and lithographic operations, use catalytic combustion incinerators, with and without heat recovery. Of the 57 plants, 8 plants are involved with gravure operations. Two of them use activated carbon solvent recovery systems, while the other six use no control devices. The two using solvent recovery systems may be classified as large plants, although not all of the nonusers can be classified as small. The airflow per press unit is in the range 3,000 to 11,000 ft^3/min, and air temperatures are about 100°F, a favorable temperature for adsorption. The airflows from the lithographic and metal decorating operations are over 300°F and generally in the 400° to 600°F range, temperatures favorable for catalytic and thermal incineration pollution control.

Duhl (1970) has analyzed the factors affecting economic recovery of gravure solvents with carbon solvent recovery systems. For an example calculation, he used an 80 press installation with total exhaust airstream of 120,000 ft^3/min at 100°F with approximate solvent load of 4,400 lb/hr. The solvent mixture being utilized was principally the acetate esters including, at times, the ethyl, isopropyl, butyl and amyl and, at times, some quantities of ethanol and propanone along with aliphatic hydrocarbons, toluene and xylene. With these solvents the concentration was of the order of 3,000 ppm. The system consisted of six Vulcan-Cincinnati Adsorbers on-stream preceded by a glass fiber filter to remove paper and dust particles, and a fin tube cooling unit to control air temperature to approximately 95°F. Economic analysis showed a recovery of $1,600,000/yr of solvent and payout time of 1.5 yr for the installation.

One of the large cost items in solvent recovery in gravure and surface coatings industries, where water soluble mixed solvents are used is the separation of the solvents from the steam condensate and from each other. For large installations where continuous and larger, more efficient, separation systems can be used the cost decreases considerably. Large installations can show a profit on solvent recovery. This may not be the case with small installations.

Other Solvent User Industries

The combined solvent emission from the remaining solvent user industries is of the order of 32 lb/da per 1,000 people based on the San Francisco Bay Area (1969) survey report. Table 1-XXII gives a partial breakdown of the industries and estimated emission rates for three groups of industries.

Table 1-XXII Amount of Solvent Emitted by Plastics, Rubber, Paper Coating and Pharmaceutical Industries

Industry	Lb/da per 1,000 people
Plastics, resin, putty mfg.	14
Surface coating, rubber products, pharmaceutical mfg.	6
Other solvent users, possibly adhesives, paper coatings, extraction of vegetable oils plastic products	12
Total	32

The solvents used in these industries have been identified, as listed in Table C-I, and are the same as used in surface coatings, and flexographic and gravure printing processes. The problems of pollutant control are also quite similar.

A number of carbon solvent recovery systems are in successful operation in fiber or synthetic filament production (plastics), rubber coatings of gloves, pharmaceuticals, adhesives and paper coatings (Vulcan-Cincinnati, Inc).

Rubber Products Industry

General - Certain raw and synthetic rubber products processing steps emit uncontrolled organic solvents and particulates into the atmosphere. In addition, pollutants are emitted in the production of certain types of synthetic rubber such as butadiene-styrene (SBR). While most of the rubber products industry consists of large operations such as tire manufacture, small specialty items are also produced. Most rubber products are processed in the same manner except for changes in compounding recipes and vulcanizing operations.

Product Processing Steps - With a few minor exceptions the manufacture of rubber products involves: compounding, mixing, forming and vulcanization. Compounding is the process of selecting and weighing the various ingredients required by the formulation and involves the selection of rubber, rubber chemicals, reinforcing pigments and processing aids. Mixing is the blending of the compounding mixture to attain dispersion of pigments and production of consecutive uniform batches. In forming process, rubber is extruded into the desired shape or calendered (applying sheeted rubber to a fabric). Rubber cementing is also a forming process in which rubber stock solvents are mixed to form an adhesive. Rubber building is the combining of stocks of different composition. Vulcanization (curing) is the last major processing step. The curing process involves application of heat to convert the green dough into an elastic state.

Emission Sources from Rubber Products Processing - Most pollutants are emitted from rubber mills used in the mixing process and in applications of rubber cements in the forming step. Particulates (dusts and fumes, oil mists) and odors are emitted. Mixing emissions vary depending on the size of the mill, size of batch and composition of the mix. Solvent vapors are uncontrolled. Large quantities of uncontrolled organic solvent vapors are also given off in the form of rubber cements (D'Imperio, 1967).

Rubber Cements - Rubber is more or less soluble in most aliphatic and aromatic solvents. The cements are made by mixing stock rubber and solvent together in churns to form a solution which will flow at 10% concentration (Rogers, 1968). Cements find application in production of products such as hospital sheeting, balloon and life raft fabrics, nipples, gloves and in part of the tire building process.

Emission Types and Properties of Rubber Solvents - The physical properties of organic solvent vapors emitted from products processing are given in Tables 1-XXIII and -XXIV. The processing solvent used varies according to the base polymer. Solvents such as benzene, toluene and xylene are used with natural and SBR rubber. Various ketones, etc., used with nitrile and neoprene synthetics. The proportion of solvent used is determined by the solvent power of the stock, consistency desired and character of the stock.

Synthetic Rubber Processing - The process for producing most synthetic rubber consists of mixing monomers of butadienestyrene (SBR). Soaps and mercaptans are added and the mixture polymerized. Oil and carbon black are then added and the mixture coagulated and precipitated from a latex emulsion. Rubber particles are dried and baled (MacGraw, 1970).

Table 1-XXIII Properties of Solvents Emitted from Natural and SBR Rubber

Solvent	Chemical formula	Density, lb/gal	Mol wt	Boiling range, °F	LEL, ppm
Benzene	C_6H_6	7.36	78	176	14,000
Naphtha(petroleum	----	5.01	--	86-140	10,000
Trichloroethene	$ClHC:CCl_2$	12.2	131	188	---
Tetrachloroethene	$Cl_2C:CCl_2$	13.5	166	250	---
Pentachloroethane	Cl_3CCHCl_2	13.9	202	324	---
Carbon tetrachloride	CCl_4	13.3	153	171	---
Toluene	$C_6H_5CH_3$	7.24	92	231	14,000
Xylene	$C_6H_4(CH_3)_2$	7.30	106	291	10,000
Kerosene	----	----	---	300-550	7,000
Diethyl ether	$C_2H_5OC_2H_5$	5.84	74	94	18,500
Gasoline	C_3H_8 to C_6H_{14}	6.68	---	100-400	14,000

Table 1-XXIV Properties of Solvent Emitted from the Synthetic Rubber Industry

Solvent	Chemical formula	Density, lb/gal	Mol wt	Boiling range, °F	LEL, ppm
2-Butanone	$CH_3COC_2H_3$	6.71	72	172-178	20,000
4-Methyl-2-pentanone	$CH_3COCH_2CH(CH_3)_2$	6.68	100	237-243	14,000
1,2-Dichloroethane	$ClCH_2CH_2Cl$	10.4	98	182	62,000

Emission Sources from Synthetic Rubber - Organic compounds are emitted from reactor and blow-down tanks; odors are emitted from the drying process.

Emission Types and Properties from Synthetic Rubber - Emission factors are presented on Table 1-XXV as given by MacGraw (1970). In the SBR process, gases are recycled, but some odors are emitted.

Pollutant Emission Control - Rubber mills have exhaust hoods to remove dusts, fumes and mists from the rolls. The most common control device is a bag house to remove particulates. Scrubbers are sometimes used to control oil mists. There does not appear to be odor control devices. In the SBR process, gases are recycled back through the process.

It is not known if any kind of air pollution equipment is used in tire retreading shops since pollutant data and emission rates are difficult to obtain in this area. It is likely that the same organic solvents are used in retreading as are used in other parts of the rubber industry.

Solvent Extraction of Vegetables

Solvent extraction is an efficient way to recover oil from seeds, such as soybean and cotton, and from lemons. Hexane or heptane is used for the seed extraction where the process may be continuous in large plants or batch-wise in the smaller ones (Cowan, 1969). A closed system is employed, keeping vapor emissions very small. A carbon resorb would be amenable to the recovery of any escaping solvent vapors.

2-Propanol is used in the extraction of lemon pulp in the plant of Exchange Lemon Products, Corona, California (Barnebey, 1965). 2-Propanol vapors escaped from the plant operation in exhaust air at 2,000 ft^3/min, 8300 ppm and 120°F. The solvent is being recovered for reuse with an activated carbon resorb system. Because of particulate matter and small amount of HCl, a liquid scrubber is used to clean the air-solvent mixture before entry into the carbon bed.

Solvent and Fuel Evaporation From Storage

Another potential emission source is the organic vapor loss from above-ground fixed-roof storage tanks, which are subject to day-night temperature fluctuations. Almost every

Table 1-XXV Emission Factors from Synthetic Rubber Plants Pounds per Ton of Product, (MacGraw, 1970)

Compound	Emissions[1]
Alkenes	
Butadiene	40
Methyl propene	15
Butyne	3
Pentadiene	1
Alkanes	
Dimethyl heptane	1
Pentane	2
Ethanenitrile	1
Carbonyls	
Propenoic nitrile	17
Propenal	3

(1) Butadiene emission is not continuous and is greatest after a batch of partially polymerized latex enters the blowdown tank.

chemical manufacturing operation has storage tanks for solvents or reactants, while the petroleum industry may be the largest user of storage facilities. For gasoline storage, 29,000 tanks are reported in use in the country, which range in size from 42,000 to 21,000,000 gallon capacity. Gasoline vapor loss from this source in the United States is estimated at 7.5 lb/da per 1,000 people. Gasoline evaporative losses of all types approach 25 lb/da per 1,000 people, which include losses from floating roof tanks and during transfer. In the San Francisco Bay Area (1969), the estimated industrial solvent evaporation rate was 5.1 lb/da per 1,000 people.

Some calculations were made which indicate that carbon adsorbent devices are feasible for this application and that further study is warranted. For a 3,360,000 gal tank, the estimated evaporation is 71,400 gal/yr, API Bulletin 2518. The concentration of gasoline vapors in the vent gas during warm-up is reported to vary from 30% to 50% by volume. If the assumptions given below are made, the intake flow during cooling is about 20 ft^3/min and out flow about 40 ft^3/min.

Mean ullage	50% of capacity
Cool-down and warm-up time	8 to 10 hr
Temperature fluctuation span	25°F

Because of the high vapor concentration, cooling of the carbon bed will be necessary. This can be done by pumping a coolant liquid through coils in the carbon bed. During the night, when air is being drawn in, the bed could be desorbed by applying heat by means of the same liquid and coils. Per adsorption phase of the cycle the gasoline weight pick-up will be about 1,200 lb, requiring from 3,500 to 5,500 lb of carbon. The amount of gasoline vented and hence the required carbon bed size will vary with the ullage and temperature change span. The main cost items will be the adsorber and carbon, refrigeration and heating. The amount of gasoline recovered will be 71,400 gal/yr which at 13¢/gal will place the recovered gasoline value at $9,000/yr. The value of the recovered gasoline reduces the overall cost of the pollution control.

Gasoline is low molecular weight, containing considerable amounts of butane and propane, hence the high or near saturation vapor pressures and the need for refrigeration in adsorption; see Table 1-IX for compositions. Industrial solvent and chemical reactions that are of higher molecular weight will be more amenable to carbon adsorption recovery systems.

Gasoline, other fuel, and solvent vapor losses can occur during transfer of the liquids between storage tanks and motor vehicle tanks due to displacement of vapors from the tank being filled. One method to prevent this type vapor loss is to install a vapor line to carry the vapors from the tank being filled to the tank being emptied. When this method is not feasible, the vapors can be recovered by a carbon resorb type system. Incineration of the escaping vapors has also been proposed.

Meat Rendering Industry

Description of Industry - Animal matter (offal) not suitable for food for either humans or pets is converted to salable products by rendering. Rendering plants are the major outlets for disposal of waste from slaughter houses, butcher shops, poultry dressers and other processors. They also dispose of whole animals that have died naturally or accidentally. In this respect, the rendering also operates as a scavenger or solid waste disposal industry.

The process is thermal and yields as main products a proteinous meal, suitable as animal feed, and tallow. Bones are also ground into the process input feed; hence the proteinous meal is enriched with calcium and phosphate.

Based on statistics given by Easton (1969) the meat and poultry industry has been growing at a rate of 5% per year since 1963 in dollar volume of business. Since the meat rendering operations are scavengers for the overall meat industry, they of necessity must also expand.

Most rendering plants are old, but some modern plants have been constructed in recent years. The older plants operate batch processes while the modern ones have converted to continuous operations such as the Anderson Carver Greenfield (Barr, 1966) or the Dupps Duke systems.

The estimated number of meat rendering plants is between 800 and 900. Average figures for the older plants indicate about 4 cookers per plant, 6 batches of offal processed per day and daily processing of about 100,000 lb. Norfolk Tallow Company, Chesapeake, Virginia reports a 20,000 lb/hr processing rate for the continuous-type plant.

Rendering Processes - The rendering process is comprized of 3 basic steps:

1. Grinding

2. Cooking

3. Separation of tallow from protein-bone meal.

The grinding breaks down the offal to a homogeneous hash which is then charged into the cooker. In the older plants the cooking is a batch process wherein a steam jacketed cooker is used. Steam temperatures at 300°F are needed to digest the bones, hooves, hides and hair, in addition to the meats and fats. Process times range from 1 to 4 hr. The moisture content of the charge is initially 40% to 50% which, during the heating phase, is reduced considerably, the steam being vented through a condenser.

The exhaust steam contains very odorous gases which are in part dissolved in the condensate and in part escape through the condenser in gas phase.

The hot digested mixture or slurry from the cooker is then discharged over a screen. Most of the melted tallow passes through, while the solids or cracklings, consisting of the digested bones and proteinous constituents, are retained. The cracklings are pressed to remove most of the adhering tallow. At this point the moisture content of the cracklings is below 8% allowing preservation without refrigeration. The tallow is filtered and then dehydrated by centrifugation, settling or air blowing.

In the Anderson Carver Greenfield system, the incoming raw material is finely ground and mixed with recycled liquid fat. In the second step, the fluidized ground slurry is pumped through a steam heated evaporator operating at 190° to 210°F and 27 in. of Hg vacuum. The released water vapor and noncondensable gases are expelled through a water cooled contact condenser. The dewatered slurry is continuously centrifuged to remove the major portion of the tallow from the cracklings and the cracklings are then run through continuous presses or expellers to reduce the tallow content.

Some materials (blood and feathers) that do not contain tallow are digested and dewatered in batch dry rendering cookers.

Pollutant Emission - Odorous pollutants escape from several locations of the older batch operated plants. Measurements were made by IIT Research Institutes (1971) to establish a semiquantitative assay on the magnitude of various plant type vapor samples. The estimates are reported in micrograms (μg) per liter of plant air in Table 1-XXVI. In the third column the concentrations have been converted to volume ppm, assuming a mean molecular weight of 90.

Table 1-XXVI Concentration of Pollutants in Plant Air At Various Operating Areas or Exhaust Vents

Area or vent	Concentration range, μg/l	ppm
Raw pile area	1.9 to 3.8	0.5 to 1.0
Cooker condenser	10.8 to 11.2	2.9 to 3.1
Cooker dump area	3.1 to 5.8	0.8 to 1.6
Press area	4.5 to 8.5	1.2 to 2.3
Press ventilator	27.4 to 50.4	7.4 to 13.7
Grease drying operation	7.7 to 9.6	2.1 to 2.6

Mills, et.al. 1967, reported estimates of odorant emissions from rendering operations in the Los Angeles area. From a survey of beef cattle operations (swine, sheep, poultry, etc. were not considered in these estimates) and assumptions of average weights of cattle and inedible refuse (mainly blood and offal), Mills calculated that plants handling refuse from 28,000 cattle would emit about 3x10" odor units per day from offal and about 5x10" odor units per day from blood. (An odor unit is the number of dilutions required to dilute the odor intensity of a unit volume to its recognition threshold concentration.)

For a batch rendering process, Mills (1967) reports total emissions and odorant emissions as a function of time during processing. Peak odor emissions take place during the first hour of operation, as shown in Figure 1-3.

The continuous rendering plant is to a considerable extent a closed system. In a well maintained plant, pollutant vapors could escape into the atmosphere only at a few locations; i.e., at the raw material receiving bins, evaporator condenser, and at the crackling or meal presses. The latter two emission points can be readily connected to pollutant control systems. Odors from the receiving bins are variable depending on the type of material being pro-

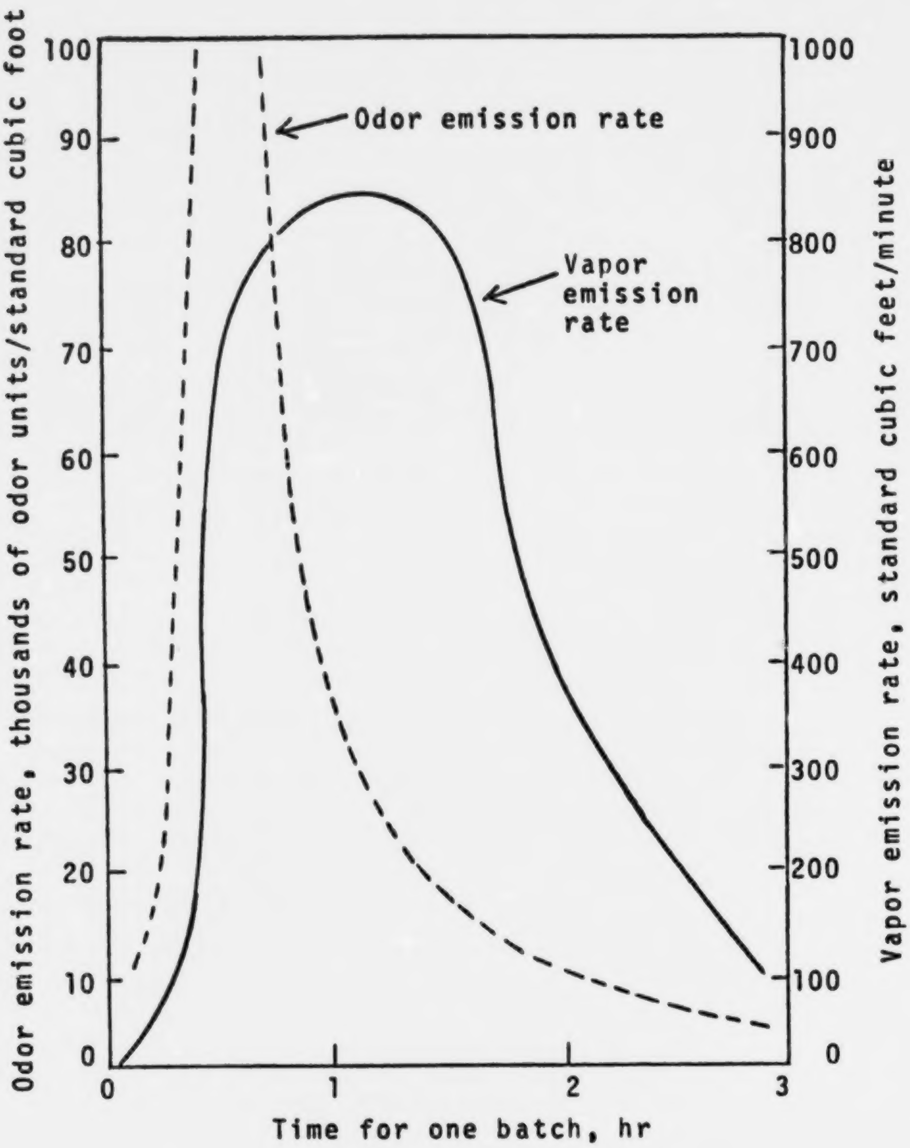


Figure 1-3 Typical Rates of Odor Emissions and of Vapor Emissions from a Batch-Type Rendering Cooker Reducing Inedible Animal Matter

cessed, age of the material and ambient temperature.

Identity of Pollutants Emitted - Table 1-XXVII lists 43 pollutant vapors that have been found in air samples from various rendering operations (Straus, 1964; IITRI, 1971). An analysis of study results conducted by IITRI (1971) give indications that the major part of pollutants are concentrated in about nine compounds. The study used the technique of dual column gas chromatography and mass spectrography. Thirty chemical compounds were identified in synthetic laboratory vapor samples prepared from prepressed cracklings, finished crackles and press grease solid samples from the Chicago rendering plants. Those compounds, as identified by the Kovats index, that were in excess of 10% of the total pollutant mixture are listed in groups in Table 1-XXVIII (Kovats, 1964). Of the nine compounds predominating in the vapor mixtures, five were identified, namely, 2-methyl propenal, 3-methyl butanal, n-hexanal, propanoic and butanoic acids. Most of the other compounds were present in fractions of a percent. IITRI did not report any amine or sulfide compounds although they qualitatively detected the latter in all samples.

Emission Control - The control of pollutant emissions from rendering plants poses a difficult problem; one that has not been solved although attempts have been made. Factors contributing to the difficulty are:

1. Low pollutant concentration, hence negligible fuel value and thereby a disadvantage in catalytic and thermal incinerations.

2. Extremely low detection levels of many of the malodorous pollutants, thereby requiring large decreases in concentrations, a task difficult to accomplish by mere dilution with additional air.

3. Release of pollutants at low concentration levels from many locations thereby requiring ducting or hooding from many locations or use of plant wide ventilation.

4. High moisture content and particulates in the exhaust air.

Operating costs have been estimated for the incineration and carbon adsorbent systems and are reported in detail in Chapter 6. The results of the estimates are summarized

Table 1-XXVII Pollutant Vapors Emitted from Meat Rendering Processes

Pollutant	Chemical formula	Mol wt	Density, lb/gal	Boiling point, °F	LEL, ppm
Difurfuryl ether	$[C_4H_3OCH_2]_2O$	178	9.5	213	---
n-Nonanal	$CH_3[CH_2]_7CHO$	142	6.9	367	---
n-Octanal	$CH_3[CH_2]_6CHO$	128	6.8	325	---
Dipropyl sulfide	$[C_3H_5]_2S$	120	6.9	287	---
n-Octane	$CH_3[CH_2]_6CH_3$	114	5.8	257	10,000
n-Heptanal	$CH_3[CH_2]_5CHO$	114	7.1	311	---
3-Methyl butanoic acid	$[CH_3]_2CH_2CO_2H$	102	7.8	350	---
Triethylamine	$[C_2H_5]_3N$	101	6.1	192	12,000
n-Heptane	$CH_3[CH_2]_5CH_3$	100	5.7	209	12,000
n-Hexanal	$CH_3[CH_2]_4CHO$	100	6.9	269	---
2,4-Dimethyl-1-3-pentadiene	$CH_2=CH[CH_3]CH=C[CH_3]_2$	96	---	---	---
Toluene	$C_6H_5CH_3$	92	7.2	231	14,000
Butanoic acid	$C_3H_7CO_2H$	88	7.9	327	---
n-Pentanol	$CH_3[CH_2]_4OH$	88	6.8	280	10,000
n-Pentanal	$CH_3[CH_2]_3CHO$	86	6.8	218	---
2-Methyl tetra hydrofuran	$\underline{O[CH_2]_3C}HCH_3$	86	7.1	172	---
n-Hexane	$CH_3[CH_2]_4CH_3$	86	5.5	156	11,000
3-Methyl butanal	$[CH_3]_2CH_2CHO$	86	6.7	166	25,000
2,3-Dimethyl-1,3-butadiene	$CH_2=C[CH_3]C[CH_3]=CH_2$	82	6.2	157	---
Benzene	C_6H_6	78	7.3	176	14,000

Table 1-XXVII (continued)

Pollutant	Chemical formula	Mol wt	Density, lb/gal	Boiling point, °F	LEL, ppm
1-Butanol	$CH_3[CH_2]_3OH$	74	6.8	244	14,000
Propanoic acid	$C_2H_5CO_2H$	74	8.3	286	29,000
Diethylamine	$[C_2H_5]_2NH$	73	5.7	133	18,000
2-Methyl propanal	$[CH_3]_2CHCHO$	72	6.6	142	16,000
n-Pentane	$CH_3[CH_2]_3CH_3$	72	5.2	97	14,000
n-Butanal	$CH_3[CH_2]_2CHO$	72	6.8	168	14,000
2-Methyl propenal	$CH_2=C[CH_3]CHO$	71	6.9	164	---
Imidazol	$\underline{NHCH=NCH=CH}$	68	---	492	---
Ethanediol	$HO[CH_2]_2OH$	62	9.3	386	32,000
n-Propanol	$C_2H_5CH_2OH$	60	6.7	206	21,000
Trimethylamine	$[C_2H_5]_3N$	59	5.5	39	20,000
n-Propanal	C_2H_5CHO	58	6.7	119	29,000
Propanone	$[CH_3]_2CO$	58	6.6	133	30,000
Propene nitrile	$CH_2=CHCN$	53	6.6	172	30,000
Methanethiol	CH_3SH	48	7.3	45	39,000
Ethanol	C_2H_5OH	46	6.6	174	33,000
Ethylamine	$C_2H_5NH_2$	45	5.7	63	35,000
Acetaldehyde	CH_3CHO	44	6.5	69	40,000
Hydrogen sulfide	H_2S	34	10.8	-76	43,000
Ammonia	NH_3	17	6.4	---	160,000
2-Butanone	$CH_3COC_2H_5$	72	7.7	305	20,000
Acetic acid	CH_3COOH	60	8.7	244	40,000
2-Propanol	$CH_3CHOHCH_3$	60	6.5	180	23,000

Table 1-XXVIII Most Abundant Pollutants in Vapor Mixtures from Crackling, Grease and Tallow During Rendering

Kovats index of pollutant	Probable chemical identity of poll.	Percentage in vapor	Description of pollutant odor
885		23	unpleasant
886	2-methyl propenal	29	aldehyde
887		20	unpleasant
923	3-methyl butanal	36	rancid
994		11	rancid
998		53	rancid
1077		15	aldehyde
1078		46	aldehyde, musty
1079		18	aldehyde, musty
1080	n-hexanal	40	aldehyde, musty
1083		13	aldehyde, musty
1087		30	aldehyde, musty
1142		12	minty, unpleasant
1415		11	unpleasant
1420		16	unpleasant
1425		19	unpleasant

Table 1-XXVIII (continued)

Kovats index of pollutant	Probable chemical identity of poll.	Percentage in vapor	Description of pollutant odor
1504	propanoic acid	15	unpleasant, soap
1509		17	unpleasant, soap
1511		26	soap
1595	butanoic acid	15	putrid, rotten
1599		10	putrid, rotten
1603		23	putrid

graphically in Figure 6-31. Results taken from Figure 6-31 show that to operate the three systems at the 10 ppm concentration level, as found in rendering operations, the costs to clean the exhaust air would be approximately as follows:

Type control system	Cost to clean exhaust air, \$/hr per 1000 ft^3/min flow
Thermal incineration	1.27
Catalytic incineration	0.95
Carbon adsorbent	0.52

Although the carbon adsorbent system can be operated at the lowest cost, there is some uncertainty that it can effect complete removal of all pollutants. As reported in Table 1-V, 28 of the 43 pollutants have V_m between 80 and 190 cm^3/mol but included in these 28 are the pollutants appearing in the exhaust airstream at the highest concentration; see Table 1-X for identity of these pollutants. No real problem is foreseen in the adsorption and desorption of the predominant pollutant vapors. 13 of the 43 pollutants, however, have V_m less than 80 cm^3/mol. Retention of some of them may be poor so an early penetration at low concentration may occur. Thermal and catalytic incinerators also operate at less than 100% efficiencies. The relative effectiveness of carbon adsorbent and incineration systems can only be determined under actual operating conditions.

Fish Rendering Industry

The main pollutants from the fish rendering operations as reported by Conrad (1971) are as given in Table 1-XXIX. The pollutants are listed downward in decreasing order of concentration and the concentration range is 1 to 12 ppb.

Table 1-XXIX Pollutant Emissions From Fish Rendering

Pollutant	Odor threshold, ppb
Dimethyl disulfide	7.6
Trimethylamine	0.2
Ethanethiol	1
Carbon disulfide	210
Propenal	210

The odor threshold (Stern, 1968) concentrations of trimethylamine and ethanethiol are of such low value that even on considerable dilution in the atmosphere after leaving the plant operating area they are still detectable.

Escape of pollutants occurs in several steps of the process, but one of the larger emission sources is the fish meal drier. Mills (1963) has reported exhaust airflow rates and odor concentrations for various fish meal input rates. To indicate the pollutant emission rate level, the exhaust gas volume for a drier of 10 ton/hr meal input rate is 18,500 ft^3/min and concentration is 1,500 odor units. If dimethyl disulfide is assumed to be the predominant odor the pollutant concentration is of the order of 10 ppm, but if the predominant odor is that of trimethylamine, the pollutant concentration is of the order of 0.3 ppm.

The problems of pollution control in the fish rendering plants are expected to parallel those of the meat rendering plants. According to Conrad (1971) the public complaints are directed mainly toward particulate emissions rather than odors from the plant. Also odors from unloading ships are subject to more complaints than from the fish processing plants.

Canning Industry

Vegetable, meat and fish canning industries have some odor problems, with the fish canning emitting the most offensive variety while the vegetable canning, the least.

Vegetable Canning - The basic source of odor comes from the blanching operation which is done as soon as possible after the vegetables have been removed from the field. This is done to facilitate preparation procedures such as removal of skin and to prevent deterioration due to the time lag between picking and canning. Although odors are emitted which could be judged objectionable by normal standards, canning plants are usually located close to the source of the vegetables in rural areas. The majority of the people in the area are employed in the industry and thus odor is accepted as a necessary factor.

Fish Canning - These canneries are located near harbors, and fish rendering plants are located near the canneries to process the by-products. Much of the odorous air pollutants attributed to canneries come from by-product processes. Only choice fish parts are canned for human consumption, the remainder being converted into by-products such as fish oil and protein animal feed supplements.

Canning preserves highly perishable fish foodstuffs. Fish are canned by two methods. In the older "wet-fish" method trimmed fish are cooked directly in the can. The newer method, "pre-cooked process", is characterized by cooking the whole, eviscerated fish, and by hand sorting of choice parts before canning.

In wet-fish canning, open cans containing the fish are conveyed through hot exhaust boxes where live steam cooks the fish. At the discharge end, cans are mechanically upended to decant stick-water (condensed steam, juices, oils), which is collected and retained for by-product processing. Cans of drained fish are filled with oil or sauce, sealed and pressure cooked.

In the precooked process (used for larger fish), whole, eviscerated fish are put in baskets and then live-steam cooked. After cooking, the fish are cooled and placed on a conveyor belt where the choice portions are picked by hand, packed and sealed into cans, and then sterilized by pressure cooking. The scraps and stick-water are collected and transferred to the rendering processes.

Air pollution from fish canning is due to the malodorous organic compounds carried out with the steam vapors vented from cookers and is also due to nonsoluble and noncondensable vapors released from the stick-water. To abate the odor release several control operations are required, the first of which is the condensing of the steam. This operation will remove some of the water soluble and condensable vapors. The remaining vapors, including varying amounts of air, may then be burned by catalytic or thermal incineration. If particulates are present, a water spray and demister are required prior to the catalytic incinerator. If air entrainment is large so that pollutant concentration is low, a carbon resorb system following the water spray and demister may be more economical.

The odor vapors have not been identified but their identification will, in this case, not be a factor in determining the effective use of a carbon resorb system. Most of the compounds in the lower part of Table C-I, up to 80 cm^3/mol V_m, would be removed by the water spray because of their water solubility. Five compounds are not water soluble - namely: methanethiol, propyne, dichloromethane, carbon disulfide and ethanethiol - but of these, carbon disulfide and ethanethiol and all those that are above 80 cm^3/mol, V_m, are adsorbed strongly enough to be removed.

Meat Canning - The processes involved in meat canning involve: (1) cooking of the meat in a sealed kettle, (2) transfer of meat from the kettle to cans, (3) conveyance of the cans through an exhaust box and (4) sealing of the cans.

Odor release occurs when the kettle is opened and during conveyance through the exhaust box. In both cases the odors are released in the presence of considerable steam. As in fish canning, condensation of the steam is the first step in pollution control, followed by incineration or adsorption of the insoluble and noncondensable gases. The factor determining whether incineration or adsorption is used is the pollutant concentration.

Restaurants

Based on the San Francisco Bay Area survey (Bay Area 1969), the estimated pollution rate from restaurants is 1.6 lb/da per 1,000 people or, for 15,000 restaurants, at a rate of 0.4 lb/da per average restaurant.

Kitchen odor emissions come from the grill and fryer, vegetable cookers and steam tables. In small operations, these are all vented through a common duct. In large operations a separate ventilation system is directed to frying and grilling, and emissions from vegetable and steam tables are controlled by the main ventilation system.

The primary source of odors is from the frying and grilling operation, but the identities of the pollutants have not been determined. Qualitatively the pollutant in the restaurant exhaust can be described as oily matter of a wide range of particle sizes, accompanied by various food volatiles and decomposition products. The predominant odor character is oily. Acrolein, a dehydration product of glycerol, is present to some extent in effluent from fat frying, but it is not the predominant odor.

A carbon resorb system can be an effective means for removing the pollutant vapors from the exhaust to the outdoors since carbon air purification systems are used in the dining areas of the restaurants to remove kitchen odors. The carbon resorb system would have to be well protected from the oily particulates by means of dry filters or wet scrubbing.

Meat Smokehouses

Control of pollutant emissions from smokehouses appear to be better controlled by thermal incineration than by sorbent systems due to two reasons: (1) the emission contains poorly adsorbed methanal, and (2) the pollutant concentration is generally in the 1100 to 1500 ppm range where the sorbent system is not economically competitive with the catalytic and thermal incineration systems. The use of thermal incinerators has not, however, been entirely successful in controlling smokehouse pollutant emissions. Pollutants identified in the emissions are as follows:

Pollutant	Concentration, ppm
Methanal	20 to 40
Higher aldehydes	140 to 180
Formic acid	90 to 175
Methanoic and ethanoic acid	460 to 500
Phenols	20 to 30
Ketones	190 to 200
Resins	1000

According to the U.S. Industrial Outlook, 1970, smoked products are being prepared chemically, hence, smokehouses may be eliminated in the near future.

Coffee Roasting

Coffee roasting is in the doubtful category. The effluents are emitted at temperatures in the 500° to 900°F temperature range and contain both particulate matter and vapors, the vapors being the lower molecular weight aldehydes, lower molecular weight organic acids, hydrocarbons and mercaptan at total concentration near 500 ppm. Under these conditions the estimated control cost with a carbon resorb system would be over \$0.80/hr per 1000 ft^3/min of gas flow. The operation would involve cooling the gas stream, particulate filtration and burning of the desorbed pollutants. Catalytic incineration, at 500°F gas temperature, would cost about \$0.80/hr per ft^3/min and about \$0.41 at 900°F gas temperature. Particulates may have to be filtered from the gas stream at the elevated temperature. Thermal incineration would cost about \$0.97/hr per 1000 ft^3/min at 500°F gas temperature and less at 900°F. The latter would have an advantage in that the particulates would also be burned to a large extent if not completely.

Tobacco Curing, Zinc Plating and Tanning

Tobacco curing, zinc plating and tanning do not appear controllable with carbon adsorbent systems operated at normal temperatures, because of the low molecular weight pollutants. The pollutants emitted by these industries are listed below:

Tobacco curing	Zinc plating	Tanning
Ammonia	Ammonia	Ammonia
Methanal		Methanal
Methanol		
Acetic acid		
Asparagine, $[H_2NC(O)CH_2CH(NH_2)COOH]$		

The ammonia is not controllable with unimpregnated activated carbon systems. A carbon impregnated with phosphoric acid will react with the ammonia, but regeneration is expected to be too expensive. In a dry airstream such as might be the case with zinc plating, a molecular sieve sorbent system would be feasible and desorption then done by heating and returning the ammonia back into the operations. The methanal and methanol are also poorly adsorbed by activated carbons, hence, competing systems or methods have been considered.

Some catalysts decompose ammonia to N_2 and H_2, a possible answer to zinc plating pollution problem, unless traces of ammonium chloride or zinc chloride poison the catalyst. A two catalyst bed would be required for tobacco curing and tanning; the second being a combustion catalyst to burn methanal and the other organics.

Control of Pollutants from Incinerators

Most of the refuse in San Francisco was burned in residential incinerators (Bay Area, 1969). For 1969, the number of reported residential incinerators was 1,080,000 which burned 2,214 tons of refuse per day. Also in use were 305 single chamber commercial incinerators which burned 15 tons of refuse per day and 744 multiple chamber commercial incinerators which burned 398 tons of refuse per day. There was a drastic difference in the amount of pollutant emitted by each type of incinerator. The reported emission factors, as given in Table 1-XXX indicate incomplete combustion in the residential incinerators, resulting in excessive emissions of organics, particulates and carbon monoxide. The use of multiple chamber commercial incinerators for the burning of all refuse appears to be one of the better solutions to the incineration pollution problem. With the latter the organic, particulate and CO emissions are reduced to very low levels.

Table 1-XXX Pollutant Emission Factors for Three Types of Incinerators

	Emission factor, lb pollutant/ton refuse				
Type	Organic	Part.	NO_x	SO_x	CO
Residential	252	24	0.1	1.0	600
Commercial, single chamber	90	8	1.0	1.0	84
Commercial multiple chamber	0.8	2.5	2.0	1.0	0.05

A carbon adsorbent system, to clean up the effluent from the residential incinerators would not be practical, because the adsorbent system would have to be operated at, (1) very adverse conditions, (2) it would not remove CO, and (3) the desorbed pollutants would have to be disposed of.

Baking and Candy Making Industries

The candy manufacturing and baking industries emit low concentrations of odors which most people do not find highly objectionable. In candy manufacture, the main source of odor comes from roasting the cocoa beans. The chemical nature of the odors are not reported in literature. The main identified emission from the baking industry is ethanol. Control of odor emissions from these two sources is not as urgent as the control of emissions from the other sources discussed previously. However, the use of incinerators for their successful control have been reported.

Other Emission Sources

The industries listed in Table 1-II account for a high percentage of the pollutant volume emitted from small stationary emission sources and also those that are of major concern because of malodorous emissions. Other existing and potential sources solvent and malodor emissions of lesser concern are recognized and are listed as follows:

Hospital exhausts
Veterinary laboratories
Cork products
Sewage vents
Perfume manufacture

Soap manufacture
Pesticide manufacturing
Cosmetic manufacturing
Fur processing
Textile finishing

Crematoria
Lagoons
Settling ponds
Stables
Fertilizer manufacture

Sulfite paper mills
Pipe coating
Asphalt air-blowing
Pharmaceuticals
Plywood manufacture

Electroplating exhaust
Azo-dye manufacturing
Waste water plants
Breweries
Distilleries

2. Environmental Effects

Introduction

The primary concern over the uncontrolled emission of air pollutants is their adverse effects on the environment. These effects range from toxicity to humans, animals and vegetation to materials damage, soiling and loss of visibility. Of paramount importance are the toxic effects on humans, resulting in mortality, morbidity, physiological and pyschological discomfort and impairment of performance efficiency. Certain pollutants have toxic effects on vegetation, leading to significant economic loss due to retarded growth, reduced yield, and, in severe instances, complete crop destruction. Other effects are damage to property, as by corrosion of metals, deterioration and soiling of architectural and other painted surfaces and discoloring and soiling of clothing and other personal effects.

Many of the adverse effects of air pollutants can be assessed in terms of real economic factors, such as health costs and dollar losses due to crop and materials damage. Other effects can only be evaluated in subjective terms, but are still significant in terms of esthetic enjoyment of life. Nontoxic, but odorous emissions arouse perhaps the most immediate and vigorous public response to pollutant emissions. Reduction of visibility is a pronounced esthetic effect of particulate and aerosol emissions and atmospheric interactions such as photochemical smog formation.

Much has been published concerning the adverse effects of air pollutants and this study has not attempted to make a definitive review of the subject. For good general reviews and related bibliography, reference may be made to the air quality criteria published by DHEW and EPA for each of the major classes of air pollutants (reference criteria documents). This study presents only a brief review of effects associated with those pollutant classes identified as being emitted by small sources and controllable by packaged devices.

The magnitude of the damage to the environment from exposure to air pollutants is dependent on two factors: the potential of the pollutants to produce the adverse effects mentioned above and the concentration of the pollutants in the atmosphere. The evaluation of these two factors, as related to emissions from small sources, is the purpose of this chapter.

Evaluation of Pollutant Concentration

The pollutant concentration that can develop in any area will depend in part on the pollutant emission rates at the various sources and in part on the air mass movements and other meteorological conditions. As indicated by the numbers given in Table 1-III, the average emission rate of all types and from all sources is approximately 5,000 lb/da per 1,000 people, with a ±30% variation for the nine densely populated areas referred to. In these, and all areas, the pollutant concentrations will vary with the prevailing meteorological conditions. For Los Angeles County and San Francisco Bay Area, the meteorological conditions are unfavorable for the dilution of pollutants in the inhabited areas. In some of the other survey areas the meteorological conditions are more favorable, but notso favorable that no effort is required to reduce the overall emission rate.

Pollutant dispersion models have been developed which allow the estimation of pollutant concentrations from point, line and area emission sources (for example, Martin and Tikvart, 1968). Considerable improvement is yet required, however, to allow realistic modeling of urban, industrialized areas, particularly where atmospheric interaction and smog formation is prevalent.

The current best estimates of pollutant concentration levels required to be protective of human health are those given in the Federal primary and secondary ambient air quality standards. Table 2-I gives the standards for six pollutants as established by the Environmental Protection Agency (EPA, April 30, 1971). The primary standard is the pollutant concentration level considered to be protective of human health, with a safety margin. The secondary standard is more restrictive in regard to SOx and particulate concentrations. It is protective also of other aspects of human welfare, i.e., protection against known or anticipated effects on soil, water, vegetation, animals and manufactured materials.

When ambient air tests show higher concentrations than allowable by the Federal standards, action is required to curb the pollutant emission rates. The identity of the pollutant very often also identifies the specific sources from which it was emitted. In other cases, the pollutants cannot be identified with a specific source, but rather to a group of sources.

Table 2-I Federal Ambient Air Quality Standards

Pollutant	Primary standard		Secondary standard	
	γ/m^3	ppm	γ/m^3	ppm
Carbon monoxide				
max 8-hr conc.(1)	10,000	9	10,000	9
max 1-hr conc.	40,000	35	40,000	35
Sulfur oxides				
annual arith mean	80	0.03	60	0.02
max 24-hr conc.(1)	365	0.14	260	0.1
max 3-hr conc.(1)	---	----	1300	0.5
Nitrogen dioxide				
annual arith mean	100	0.05	100	0.05
Photochemical oxidants				
max 1-hr conc.(1)	160	0.08	160	0.08
Hydrocarbons				
max 3-hr conc.(1) 6 to 9 AM	160	0.24	160	0.24
Particulates				
annual geometric mean	75	----	60(2)	----
max 24-hr conc.(1)	260	----	150	----

(1) This concentration is not to be exceeded more than once a year.

(2) This number is to be used as a guide in assessing implementation of plans to achieve the 24-hr standard.

Table 2-II, based on the survey results of the three California air pollution control districts (Table 1-III), shows the relative portions of the main classes of pollutants which might appear in any control district. In these survey results, 84% of the pollutants are emitted from motor vehicles. The amount of pollutants from this source can be expected to be proportional to the population density. The pollutants emitted from the stationary sources (15% of total) will also be influenced to a considerable degree by the industrialization of the area.

Table 2-II Relative Amounts of Pollutants Emitted From Various Sources (California 1969)

Pollutant	%	Source
CO	67	Motor vehicles
	4	Stationary
SO_2	nil	Motor vehicles
	3	Stationary
NO_x	5	Motor vehicles
	2	Stationary
Organic vapors	12	Motor vehicles
	3.5	Small emission
	2.5	Other stationary
	99	

The total organic vapor emission is 18% of which 12% is from motor vehicles. These are combustion products, hence will contain high proportions of aldehydes and organic acids. The 2.5% other-stationary-source emissions are primarily from incinerations of various types. In this case also, the pollutants will be to a large extent aldehydes and organic acids. The major part of the small-sources emissions are the solvents from surface coatings and other users, as discussed in Chapter 1, and will consist of halogenated hydrocarbons, toluene, xylene, ketones, alcohols, esters and ethers. The 3.5% also includes motor fuels emitted into the atmosphere during marketing.

It is evident that the organic pollutants from motor vehicles will tend to be widely distributed in proportion to population density. Pollutants emitted from small sources, although smaller percentage-wise, can create higher concentrations in local areas and produce toxic effects, damage to property and plants, and nuisance effects because of bad odors. On diluting into the atmosphere these pollutants can combine with the organic pollutants (and NO_x) from the other sources to raise the concentration level over wider areas, thereby contributing to smog formation.

Toxic Effects on Humans

The potential of a pollutant to produce a toxic effect on humans can be evaluated by two systems. One of these is the threshold limit value (TLV) and is the maximum airborne concentration of a substance to which it is believed that nearly all workers can be repeatedly exposed day after day without adverse effects. The other is the vapor irritant-grade number, and consists of five numbers which indicate the severity of symptoms felt when exposed to a vapor. The grade numbers are defined as follows:

Grade 0	Chemicals that are nonvolatile, or the vapors which are nonirritating to the eyes and throat.
Grade 1	Chemicals that cause a slight smarting of the eyes or respiratory system if present in high concentrations. The effect is temporary.
Grade 2	Chemical vapors that cause moderate irritation, such that personnel will find high concentrations unpleasant. The effect is temporary.
Grade 3	Moderately irritating volatile chemicals such that personnel will not usually tolerate moderate or high vapor concentrations.
Grade 4	Severe eye or throat irritants, vapors which are capable of causing eye or lung injury, and which cannot be tolerated even at low concentrations.

Table 2-III lists the pollutants, identified with small sources, in order of decreasing toxicity as measured by increasing TLV and decreasing vapor irritant grade number.

Table 2-III Ranking of Pollutants in Decreasing Order of Toxicity to Humans

Pollutant	TLV, ppm	Vapor irritant grade No.	Industry
Propenal	0.1	3	6,52,54
Ethanethiol	0.5	-	51,52
Ethanolamine	3	2	7
Methanal	5 (1)	2	57,60,61,63,65
Hydrogen chloride	5 (1)	3	65
Methanoic acid	5	3	57,61
Sulfur dioxide	5	3	6,63
Nitrogen dioxide	5	3	63
Phenol	5 (2)	3	55,61
Trimethylamine	10	3(3)	51,52
Tetrachloromethane	10 (2)	3	6,7
Ethylamine	10	-	51
Ethanoic acid	10	2	4,51,55,57,61,63
Methanethiol	10 (1)	2	51,55
Hydrogen sulfide	10	3	51,52
Carbon disulfide	20 (2)	2	52
Propanenitrile	20	4	6,51
2,6-Dimethyl-2,5-heptadien-4-one	25	2	4,7
3-Octanone	25	1(3)	4
Triethylamine	25	2(3)	51,52
4-Methyl-3-penten-2-one	25	2	1,4
Diethylamine	25	3	51
Benzene	25	2	1,4,6,7,51
2-Methoxy-ethanol	25 (2)	2	1,4,7
1-Nitropropane	25	1(3)	1,4,7
2-Nitropropane	25	1	1,4,7
4-Methyl-2-pentanol	25 (2)	2(3)	1,4
Ethanenitrile	40	1	6
2.6-Dimethyl-4-heptanone	50	2	1,4,5,8
Hexyl acetate	50	-	4
2-Butoxy-ethanol	50 (2)	-	1,4
4-Hydroxy-4-methyl-2-pentanone	50	1	4,7
1,2-Dichlorobenzene	50	1	4,7,51

(1) Ceiling limit, not to be exceeded
(2) Includes skin adsorption
(3) (NFPA) 1969 ratings

Table 2-III (continued)

Pollutant	TLV, ppm	Vapor irritant grade No.	Industry
Cyclohexanol	50	1	1,4
Cyclohexanone	50	3	1,4,6,7
Cyclohexane	50	1	1,4,7
2-Furyl methanol	50	1	4
1,2-Dichloroethane	50	2	6,7
2-Methyl pentyl acetate	50	1(3)	4
Ammonia	50	3	51,57,60,63,65
Pentyl acetate	100	1(3)	1,4,7
α Pinene	100	0	1,4
2-Ethoxyethyl acetate	100(2)	2(3)	1,4,5,8
2-Hexanone	100	-	1
4-Methyl-2-pentanone	100	-	1,4,5,6,7,8
Ethyl benzene	100	2	1
Xylene	100	2	1,4,5,6,7,8
1-Pentanol	100	1	1,4,51
Tetrachloroethene	100	3	2,3,6,7
1-Butanol	100	1	1,4,7
2-Methyl-2-propanol	100	1	4
Trichloroethene	100	2	2,3,6,7
Nitroethane	100	1(3)	1,4,7
Nitromethane	100	1(3)	1,4,7,55
Mineral spirits	100	1	1,4
2-Methyl-2-butanol	100	1	4
Butyl acetate	150	1	1,4,7
2-Butanol	150	1	1,4
1-Methyl-propyl acetate	150	1	1
Propyl acetate	200	1	1,4
Toluene	200	2	1,4,5,6,7,8,51
2-Pentanone	200	2(3)	1,4
Tetrahydrofuran	200	2(3)	7
1-Propanol	200	1	1,4,7,51
Methyl acetate	200	1	1,4,7
Ethanal	200	3	51
2-Ethoxy-ethanol	200	2	4,5,7
2-Butanone	200	1	1,4,5,6,7,8,51
Stoddard solvent	200	-	3
Isopropyl acetate	250	1	1,4
1,1,1-Trichloroethane	350	2	2,4
Ethyl acetate	400	1	1,4,7,8

Table 2-III (continued)

Pollutant	TLV, ppm	Vapor irritant grade No.	Industry
Diethyl ether	400	2	1,6,7
2-Propanol	400	1	1,4,7,9,51
Hexane	500	0	1,4,6,7,9,10,51
Octane	500	1	1,4,6,10,51
Heptane	500	1	1,4,5,6,7,9
Diisopropyl ether	500	2(3)	1,4
Dichloromethane	500	2(3)	2,5,7
Naphthas	∿500	1	2
1,1,2-Trichloro-1,2,2-trifluoroethane	1000	-	2,3
Pentane	1000	1	4,6,10,51
2-Methyl-butane	1000	-	10
1,3-Butadiene	1000	2	4,6
Propanone	1000	1	1,4,5,7,51,61
Propane	1000	1	10,57
Ethanol	1000	1	1,4,5,7,51,52,58
Propene	4000	1	57
Propyne	4000	1(3)	4

The TLV values are from MCA (1970) and ACGIH (1970) and the vapor irritant grade number from Committee on Hazardous Materials (1970). The last column in the table identifies the pollutant with the industry from which it was emitted; see Table 1-II for industry identification.

The most toxic pollutants, up to 20 ppm TLV, are emitted predominantly from the processing industries, namely: the meat rendering, fish rendering, coffee roasting, tobacco curing, tanning, meat smokehouses, zinc plating and also domestic incinerators. Two solvent user industries, the rubber products and adhesives, also emit pollutants in this TLV range. Several other pollutants of lower toxicity (triethylamine, benzene, 1,2-dichlorobenzene, ammonia and 1-pentanol) are also emitted from the process industry. The pollutants of lesser toxicity, i.e., with TLV larger than 20 ppm, are predominantly emitted from the solvent user industries; namely, the surface coating, degreasing, dry cleaning, graphic arts, etc.

The most toxic pollutants are emitted by industries which, on the per 1,000-population basis for the control district, have the lowest emission rates. However, the local areas under adverse meteorological conditions can experience toxic effects.

A comparison of the TLV values with the Federal standard of 0.24 ppm for hydrocarbons indicates a very large safety factor for the Federal standard in regard to toxicity. The hydrocarbon standard is based solely on the relationship of nonmethane hydrocarbon concentration to the resulting photochemical oxidant levels. Correlation of the 6 to 9 AM nonmethane hydrocarbon levels with the peak oxidant levels show an approximate three to one relationship. Thus, to maintain a standard of 0.08 ppm oxidant, the nonmethane hydrocarbon concentration should not exceed 0.24 ppm.

Odor Effects

Psychological and Physiological Effects

Odors may affect humans in different ways depending not only upon the characteristics of the odor, but also on the individual and his environment. Odors, per se, are not the cause of organic diseases or toxic effects. Some highly toxic gases, such as hydrogen sulfide, are associated with highly offensive odors, but the dangerous properties do not come from the odor itself. In this case, the odor serves as a warning of the presence of a harmful gas. Conversely, some toxic gases may be odorless or have pleasant odors.

Odors can, however, aggravate attacks of asthma and other allergic conditions which cause loss of appetite, lowered water consumption, breathing difficulties, nausea, vomiting and insomia (Sullivan, 1969). Asthmatic attacks can be triggered by odors from hay, mustard, animal skins, fermentations, paint, sulfur and cooking (Horesh, 1966). Malodorous gases are harmless to the average individual, but these gases can set off an allergic attack in sensitized people. Horesh (1966) reviewed the importance of the role of odors in the management of allergic diseases and reported that odorous irritants are significant factors in asthma, hay fever, eczema, migraine, rhinitis, allergic croup, tracheitis, dermatitis and gastrointestinal allergy. Additional substances incriminated as aggravating allergic illnesses include odors from turpentine, dimethyl sulfide, gas fumes, cleaning fluid, kerosene, newspaper print, fish, formaldehyde and rubber. It is apparent that many gaseous odors are involved in allergic responses and can be considered as indirectly toxic.

Ranking of Pollutants According to Odor Response

Odors may be ranked on the basis of detection and threshold concentration and recognition threshold concentration. The latter method is used by odor investigators more frequently and values for more odor compounds are readily available. The more odorous pollutants emitted from small sources are listed in Table 2-IV according to increasing recognition threshold concentration, or decreasing odor response. The values for this table were obtained from Copley (1970) and Leonardos (1969).

The ranking of odorous emissions by recognition threshold concentration provides only a partial measure of the objectionable nature or perceived effect on human subjects. The odor quality has significant bearing on the subjective response or odor perception. Psychological differences in exposed humans tend to obscure this differentiation, however, since what is objectionable to one individual may elicit a different response from another.

Other properties of odorous emissions have been used for ranking or differentiation. Moncrief (1968) attempted to differentiate odors by subject acceptability. Certain compounds were generally unacceptable: mercaptans, sulfides and amines. Individual differences tended to limit the ranking of other compounds.

The human response to odor sensations may be quantitatively expressed by the Weber-Fechner law which states that

$$I = k \ln c$$

where I is the intensity of the odorant, k is a constant and c is the odorant concentration. The usual method of utilizing this expression is by human panel testing of dilution ratios. The constant in the Weber-Fechner expression is a measure of the pervasiveness of the odorant (Sullivan, 1969). Extremely pervasive odors are those whose odor intensity remains unchanged or shows only slight change (small k values) on dilution. The intensity of an odor is generally expressed in 'odor units' which gives the number of dilutions required to reduce the odor to its recognition threshold concentration level.

Additional factors which limit the characterization of odors by human response are olfactory fatigue and odorant mixtures. Olfactory fatigue is a well recognized phenomenon by which odor perception is lessened or in some instances completely inhibited by prolonged exposure.

Table 2-IV Ranking of Pollutants in Decreasing Order of Odor Recognizability

Pollutant	Odor quality	Recognition threshold, ppm	Industry
Trimethylamine	fish	0.0002	51,52
Hydrogen sulfide	cabbage	0.0004	51,52
Butanoic acid	sour	0.001	51
Ethanethiol	earthy	0.001	51,52
Nitrobenzene	shoe polish	0.004	---
Dimethyl sulfide	vegetable	0.02	---
Dipropyl sulfide	---	0.01	51
Methanethiol	---	0.02	51,55
Methylamine	fish	0.20	---
Carbon disulfide	rotten egg	0.20	52
Pentyl acetate	pears	0.1	1,4,7
Furfural	new bread	0.2	---
Propenal	burnt, sweet	0.2	6,52,54
4-Methyl-2-pentanone	sweet	0.5	1,4,5,6,7,8
Xylene	---	0.5	1,4,5,6,7,8
Dimethylamine	fish	0.5	---
Sulfur dioxide	cabbage	>0.03	6,63
Methanal	pungent	1.0	57,60,61,63
Butyl acetate	---	>0.6	1,4,7
Phenol	hay-like	1	55,56
1-Butanol	sweet	1	1,4,7
Ethanoic acid	vinegar	1	4,51,55,57,61
Nitrogen dioxide	irritating	1 to 4	63
Isobutyl acetate	---	4	1,4
Tetrachloroethene	---	5	2,3,6,7
2-Pentanone	---	8	1,4,6,7
Butanone	sweet	10	1,4,5,6,7,8,51
Gasoline	---	10	50
Propenenitrile	onion	1 to 20	6,51
Propyl acetate	pears	20	1,4
Dichloromethane	---	21	2,5,7
Tetrachloromethane	---	21	6,7
2-Ethoxy-ethanol	---	25	4,5,7
Ethanol	---	10 to 25	1,4,5,7,51,58
Mineral spirits (aliphatic)	---	30	1,4
Propenol	---	30	---
Tetrahydrofuran	---	30	7
Benzene	---	3 to 60	1,4,6,7,51

Table 2-IV (continued)

Pollutant	Odor quality	Recognition threshold, ppm	Industry
2-Methyl-1-propanol	---	40	---
2-Propanol	---	40	1,4,7,9,51
Ethyl acetate	fragrant	50	1,4,7,8
Ammonia	pungent	47	51,57,60,63
2-Methoxy-ethanol	---	60	1,4,7
Isopropyl acetate	pears	30	1,4
Trichloroethene	---	20 to 80	2,3,6,7
2-Propanone	---	100 to 300	1,4,5,7,51,61
Octane	---	150	1,4,6,10,51
Heptane	---	220	1,4,5,6,7,9
Methanol	---	100	1,4,7,55,57
Methyl acetate	fragrant	200	1,4,7
Dichloromethane	---	150 to 200	2,5,7
1,1,1-Trichloroethane	---	400	2,4

Odor intensities, as measured by human panel response, vary widely when mixed odors are used. Rosen, et.al. (1962) investigated the odor perception of mixed odorants and found that intensities of mixed systems may exhibit a variety of interactions. Intensities may be additive, counteractive, synergistic, or independent. Data on odor interactions of butanol, p-cresol and pyridine are shown in Table 2-V.

The most malodorous pollutants are emitted from the process industries, primarily the meat and fish rendering. Many of the odorous pollutants at the top of the list are also at the top of the list in Table 2-III for their toxicity, although odor is not the cause of toxicity. Except for ammonia, methanol, propanone, and methanol, the less malodorous pollutants are emitted from solvent user industries. Under adverse meteorological conditions, local areas near rendering, coffee roasting, tobacco curing, tanning and meat smokehouse operations can experience periods of malodors.

A comparison of the recognition threshold concentrations in the upper part of Table 2-IV with the Federal standard of 0.24 ppm for hydrocarbons indicates that standard is not restrictive enough, assuming the term hydrocarbon refers to all organic pollutants. A fair number of the pollutants have recognition threshold concentrations considerably below 0.24 ppm. As mentioned above, the Federal standard is based solely on health effects and does not take odor into consideration. The Air Quality Criteria for Hydrocarbons (NAPCA Publication AP-64, March 1970) concludes that, hydrocarbons, per se, do not exhibit adverse health effects at the usually occurring ambient air concentration levels.

Table 2-V Odor Interaction in Mixtures

Test	Butanol	p-Cresol	Pyridine	Total* Mixture
	Fraction of Odor Threshold Concentration at Which Odor was Perceived			
1	0.46	--	0.53	0.99
2	0.37	0.14	0.42	0.93
3	0.35	0.40	--	0.75
4	0.24	0.19	0.29	0.72
5	0.18	0.21	0.21	0.60
6	0.15	0.09	0.26	0.50
7	0.12	0.21	0.07	0.40

$$\text{*Total mixture} = \frac{\text{total concentration}}{\text{additive threshold concentrations}}$$

Odor Control

Concentration Reduction Methods - Odor control is a term which may be used to describe any process which makes olfactory experiences more acceptable to people. This can be done by reducing the odor intensity or concentration, or by odor modification. Concentration reduction by sorption devices is the main theme of this handbook (Chapters 4 and 6) with additional attention, in decreasing order of importance, also given to catalytic and thermal incineration

(Chapters 5 and 7). Concentration reduction by dilution with increased air volumes is practiced by many industries, but it is not a satisfactory solution to the problem.

Odor Modification - It is possible to nullify the perceptual response to a malodorous pollutant by the admixture of another odorous vapor into the atmosphere. This is commonly done by spraying aerosols to control, or mask, malodors coming from cooking, from densely occupied living quarters, bathrooms, locker rooms, etc. Odor modification is also being tried on a larger scale in industry, as in metal decorating operations; see Chapter 1 under Emission Control for Graphic Arts Industry.

There is no generally accepted physiological mechanism to explain odor modification. It has been shown that nasal inspiration of malodors with masking odors does not prevent the person from smelling the malodor upon being transferred to a new environment; hence, the mechanism cannot be attributed to olfactory anesthesia (AIHA, 1960).

The method has some apparent advantages in industrial applications associated primarily with low initial equipment costs. It does not counteract toxic, corrosive and smog-forming potential of the pollutants and is therefore limited in its application.

Toxic Effects of Pollutants on Vegetation

The only (nonsmog) organic pollutant capable of causing plant damage at low concentrations (less than 1 ppm) is ethene. Other organic pollutants must be present at much higher concentrations to produce equivalent plant damage. Concentrations of the order of magnitude required are highly improbable from the small emission sources.

Exposure to 0.1 ppm of ethene produces epinasty (downward bending of leaves and other plant parts). Abeles and Gahagan (1968) found that 0.1 ppm of ethene produced partial abscission (shedding of plant parts). This plant response was also studied with other hydrocarbons. These findings are combined with those of other investigators (Crocker, 1935; Zimmerman, 1935; Heck and Pires, 1962 and Burg and Berg, 1967), and are presented in Table 2-VI. These are the most active hydrocarbons and, as the results show, they must be present in concentrations of two or more magnitudes higher than ethene to produce an equivalent effect.

Table 2-VI Relative Concentrations of the More Reactive Hydrocarbons That Produce Biological Response Similar to That Produced by Ethene

			Inhibition of growth	
Hydrocarbon	Abscission	Epinasty	Pea stem	Tobacco
Ethene	1	1	1	1
Propene	60	500	100	100
Propyne	1,250	500	2,800	100
1-Butene	100,000+	500,000	270,000	2,000
1,3-Butadiene	100,000+	---	5,000,000	---

The inorganic acidic pollutants SO_2, H_2S and NO_2 have the capacity to damage vegetation. Concentrations higher than 0.1 ppm of the sulfur compounds can cause injury, while slightly higher concentrations of NO_2 are required. Sulfur dioxide is emitted from the rubber products and sulfite paper industries and domestic incinerators. Hydrogen sulfide is emitted from the rendering operations and NO_2 from commercial incinerators. The contribution from the small emission sources compared to the total emission of these pollutants from other sources (power plants, motor vehicles, etc) is very small. Local effects may occur under unfavorable meteorological conditions.

Synergistic effects of mixed air pollutants can often result in increased plant damage over that observed for the single pollutants. Examples of such synergism are given by Hindawi (1971).

Smog products, primarily ozone and peroxyacetyl nitrate (PAN) are principal contributors to economic crop loss in such affected areas as Southern California.

Excellent descriptions of the types and manifestations of vegetative response to air polluants are given in the Handbook of Effects Assessment (Lacasse and Moroz, 1969).

Damage to Materials

Observable corrosive action occurs on unprotected ferrous metals with SO_2 at concentrations less than 0.1 ppm. Nonferrous metals corrode at higher concentrations. In both cases the corrosion rate increases with increased concentration, temperature and humidity. The presence of particulates is also a corrosion rate increasing factor.

Paper and leather are oxidized to sulfates and some textiles are weakened. Sulfur dioxide and hydrogen sulfide discolor painted surfaces. Dyes are faded by nitrogen dioxide.

Clothing can be soiled by the pervasive odor emitted from rendering plants. Otherwise, organic pollutants are not considered as particularly damaging to materials.

The contribution from the small emission sources compared to the emission of these pollutants from other sources (power plants, motor vehicles, etc) is very small. Their effects will be felt locally, near the emission sources under adverse meteorological conditions.

Smog Forming Potential of Pollutants

Nature of Smog

A haze or mist, which appears to be a combination of smoke and fog, is produced photochemically when certain organic vapors in the atmosphere are exposed to solar radiation in the presence of nitrogen oxides. The products of the photochemical reactions have been identified as oxidant (ozone), nitrogen dioxide, peroxyacetyl nitrate (PAN), peroxybenzoyl nitrate (PBzN), methanal, particulates, aerosol, and H_2SO_4 mist. These substances produce eye irritation, plant damage, reduced visibility, material damage, injury to health and a characteristic odor. The H_2SO_4 mist is evidence that SO_2 is also a contributor to smog formation.

These effects are not produced by the primary contaminants, but appear after the photochemical oxidation has taken place. All pollutants are not equally active and also produce different smog effects. For example, the eye irritating smog is not the same as the plant toxicant, as evidenced by the fact that the half-life of the two effects are different. Therefore, it is important to rate pollutants according to their role as smog precursors as well as their direct irritant or nuisance effects as discussed in the previous text.

Distribution of Smog Forming Pollutants

Smog producing pollutants are ever-present where the population densities are high because the main source is motor vehicles. Table 2-VII designates the type, source and rate of the smog active pollutant emissions as calculated from the California (1969) survey results. The estimated emission rates of active organic and NO_x pollutants from motor vehicles are 360 and 200 lb/da per 1,000 people, respectively, and by far the largest emissions from any source. Heavy smog can always form where the meteorological conditions are unfavorable for the dispersion of pollutants. Where appreciable air mass movements occur, the smog thins out over a larger region. Ultimate disposal of the smog can be by a slow absorption into vegetation and terrain or by the rapid scrubbing action of rain.

Table 2-VII Sources of Smog Forming Pollutants of High and Low Activities

Type and source of pollutants	Emission rate, lb/da per 1,000 people		Percentage of organic pollutants
	High(1) activity	Low activity	
Organic from motor vehicles	360	160	46 20
Organic from solvent users and fuel marketing	35	110	4 14
Organic from other stationary sources	20	100	3 13
Organic totals	415	370	100
NO_x from motor vehicles	200	---	---
NO_x from stationary sources	95	---	---

(1) High activity refers to all olefins, substituted aromatics and aldehydes.

The rate of smog active pollutant emission from the solvent user industries is low compared to that from motor vehicles, being only 35 lb/da per 1,000 people. The effects will also be felt regionally rather than locally because: (1) a time lapse occurs during which the organic pollutant mixes in with NO_x from other sources, (2) the photochemical reactions are slow, allowing the air mass movements to carry the mixtures over a large region before the reactions are completed, and (3) emissions produced during nondaylight hours are dispersed and then react during the daylight hours.

A typical polluted atmosphere may have NO_x and total organic pollutant concentrations of the order of 0.5 ppm for each. Los Angeles (in 1970) defined a day of photochemical smog as one in which the average oxidant level is 0.10 ppm for 1 hour.

Active Smog Precursors

The smog forming potential exhibited by organic pollutants has been related to the pollutant chemical structure by the investigators in the Los Angeles County pollution control districts. Those classified as highly active are all of the olefins, substituted aromatics, aldehydes and ketones having a branched hydrocarbon structure. This method of classification is the basis for the separation of high activity and low activity groups in Table 2-VII. The percentage of high activity pollutants emitted from motor vehicles (only) is 69%, while from the solvent users and other stationary sources the percentages are 24 and 17, respectively.

Of the 167 pollutants listed in Table C-I (Appendix C), 41 can be classified as being highly active smog precursors. These are listed in Table 2-VIII with a separation made for those emitted from the solvent user industries and those from the process industries. The emissions from the process industries are small, and hence do not make a significant contribution to smog formation. Those from the solvent user industries, and including fuel evaporation, contribute about 8% of all the active organic pollutants. Of the 20 solvents listed, toluene, xylene and trichloroethene are emitted at the highest rates; hence, these three solvents are the main contributors to smog from the small emission sources. There is a sizable number of lower activity smog precursors which make a lesser contribution.

Ranking of Smog Precursors

There are several reactivity classification systems derived from different sets of data and experimental conditions. Of these, a reactivity scale based primarily on product yields and biological effects was proposed by Altshuller (1966) and Levy (1970). Altshuller took into consideration the parameters: ozone or oxidant yield, peroxyacetyl nitrate (PAN) yield, methanal yield, aerosol formation, eye irritation and plant damage. Levy included the parameters: nitrogen dioxide concentration, oxidant concentration, eye irritation, and methanal concentration. These were combined into a single system which rated pollutants from 0 to 3 in increasing order of activity. This system was further modified by MSA Research Corporation by expanding the numerical span to 0 to 10.

Table 2-VIII Pollutants From Small Emission Sources That Are Active Smog Precursors

Pollutants from solvent-user industries and fuel marketing	Process industries
2,6-Dimethyl-4-heptanone	Nonanal
2,6-Dimethyl-2,5-heptadien-4-one	Octanal
Butyl benzene	Difurfuryl ether
αPinene	Heptanal
2-Methyl-2-hexanone	2,4-Dimethyl-1,3-pentadiene
2,4-Dimethyl-3-pentanone	2,3-Dimethyl-1,3-pentadiene
Isopropyl benzene	Hexanal
Propyl benzene	3-Methyl-butanal
4-Hydroxy-4-methyl-2-pentanone	Pentanal
4-Methyl-2-pentanone	1-Pentene
Xylene	Phenol
Ethyl benzene	2-Methyl-propanal
αChlorotoluene	Butanal
4-Methyl-3-penten-2-one	1-Butene
Toluene	2-Methyl-propenal
3-Methyl-2-butanone	Propanal
2-Furyl-methanol	Propene
1,3-Pentadiene	Propenal
Trichloroethene	Propenoic nitrile
1,3-Butadiene	Ethanal
	Methanal

The expanded rating system was used to rank pollutants from small emission sources; the ranking is presented in Table 2-IX. Only a limited number of the pollutants could be ranked because of lack of complete data (data from Levy, 1970). The most active pollutants are predominantly the ketones having a branched hydrocarbon structure, olefins, substituted aromatics, and aldehydes, in agreement with the classification system used by the California investigators. Three of the most abundantly emitted solvents, xylene, trichloroethene and toluene, are in the upper part of the ranking list. In the degreasing industry, 1,1,1-trichloroethane with a relative reactivity of one is promoted as a substitute for trichloroethene with a relative reactivity of 6. Benzene is quite nonreactive; substitutions producing xylene and toluene greatly increase the reactivity.

Effect of Smog on the Environment

The effect of smog on the environment is observed as reduction in visibility, eye irritation and damage to vegetation. Eye irritation and vegetation damage are two criteria for determining the pollutant reactivity as smog precursors used in Table 2-IX ranking. Different pollutants do not produce the same type of smog; some smogs cause more eye irritation while others cause more plant damage. Table 2-X lists the classes of organic pollutants in order of decreasing activity to produce eye irritant or vegetation damaging smogs.

The most active precursors producing eye irritant and vegetation damaging smogs are xylene, 4-methyl-3-penten-2-one, 1-pentene, 1-butene and propene emitted mostly from the solvent user industries and fuel storage evaporation. Diolefins such as 2,6-dimethyl-2,5-heptadien-4-one, butadiene, 1,3-pentadiene and 2,4-dimethyl-1,3-pentadienes are only highly reactive in producing eye irritant smog. Most of the latter are also emitted from solvent user industries. The largest contributor, also volume-wise, is xylene.

Epidemiological studies conducted primarily in Los Angeles and San Francisco have attempted to ascertain the existence of correlations of respiratory illnesses, eye irritation, and other health effects with oxidant level. These have been reviewed in NAPCA Publication No. AP-63 (March 1970). The general conclusions are that the threshold for observable health effects is about 0.15 ppm oxidant. The highest correlation of effect with oxidant concentration is found for eye irritation. Excess mortality, hospital admissions, and respiratory cancer in the general public have not shown significant correlation with oxidant levels.

Table 2-IX Pollutant Reactivity Ranking As Smog Precursors

Pollutant vapor	Relative reactivity, 0 to 10 scale	Industry
4-Methyl-3-penten-2-one	8	1,4
1-Butene	7	10
Propene	7	57
Xylene	7	1,4,5,6,7,8
1-Pentene	7	10
4-Methyl-2-pentanone	6	1,4,5,6,7,8
Trichloroethene	6	2,3,6,7
1,3-Butadiene	6	4,6
Toluene	6	1,4,5,6,7,8,51
4-Hydroxy-4-methyl-2-pentanone	6	4,7
2,6-Dimethyl-4-heptanone	6	1,4,58
2-Ethoxy-ethanol	6	4,5,7
2,6-Dimethyl-2,5-heptadien-4-one	6	4,7
1-Methyl-1,4-epoxybutane	6	4,51
Isopropyl benzene	6	1,10
Ethyl benzene	6	1
Ethene	5	---
Butyl benzene	4	1
Cyclohexane	4	1,4,7
Cyclohexanone	3	1,4,6,7
Butanone	3	1,4,5,6,7,8,51
Methanol	3	1,4,7,55,57
2-Propanol	3	1,4,7,9,51
Butanol	3	1,4,7
Diethylamine	3	51
Triethylamine	3	51,52
Propanone	2	1,4,5,7,51,61
Ethyl acetate	2	1,4,7,8
Butyl acetate	2	1,4,7
Ethanol	2	1,4,6,10,51
Benzene	1	1,4,6,7,51
Nitropropane	1	1,4,7
1,1,1,-Trichloroethane	1	2,4
Pentane	0	4,6,10,51
Propane	0	10,57

Table 2-IX (continued)

Pollutant vapor	Relative reactivity, 0 to 10 scale	Industry
Propyne	0	4
2-Ethoxy-ethyl acetate	0	1,4,5,8
Ethanediol	0	4,51
Phenyl acetate	0	1,4,7
1,1,2-Trichloro-2,2,1-trifluoroethane	0	2,3

Table 2-X Ranking of Organic Pollutants Producing Eye Irritant and Vegetation Damaging Smogs (Data from Altshuller, 1966)

Compound or compound class	Response on 0 to 10 scale	
	Eye irritation	Vegetation damage
Internally double-bonded olefins	4 to 8	10
Dialkyl and trialkyl benzenes	4 to 8	5 to 10
1-Alkenes	4 to 8	6 to 8
Diolefins	10	0
Ethene	5	+(1)
Toluene and other monoalkyl benzenes	4	0 to 3
Aliphatic aldehydes	+(1)	1(1)
Paraffins	0	0
Benzene	0	0
Acetylene	0	0

(1) Effect noted experimentally, but data insufficient to quantitate.

Barth, et.al. (1971) report a study which indicates the eye irritation threshold as being about 0.1 ppm oxidant. The time to cause barely perceptible eye irritation, based on human panel testing of synthetic smog, is four minutes.

Pollutant Regulatory Laws

Federal Standards

The purpose of the pollutant regulatory laws is to control emission sources so that ambient air in inhabited areas is not injurious to health, vegetation, or property, nor detracts from enjoyment of life. Acceptable concentration levels that permit attainment of the above requirements have been established by the Environmental Protection Agency (EPA, April 30, 1971) for six types or groups of pollutants; namely, carbon monoxide, sulfur oxides, nitrogen dioxide, photochemical oxidants, hydrocarbons, and particulates. The established concentration levels are given in Table 3-I. For carbon monoxide the established level is of the order of 10 ppm, while for the other gaseous pollutants it is of the order of 0.1 ppm.

The primary standards, in Table 3-I, are the pollutant-concentration levels considered to be protective of human health, with a safety margin. These standards are to be attained in three years starting April 30, 1971. The secondary standards are more restrictive in regard to sulfur dioxide and particulate concentrations and are to be attained in 27 additional months. These standards are, however, subject to changes as more knowledge becomes available on health and welfare effects.

States were required to adopt and submit plans to the EPA by Jan. 30, 1972, which will maintain and enforce the Federal ambient air quality standards in each air quality-control region. The regions have been established by the EPA and were determined on the basis of population, climate, topography, and geography.

Control District Regulations

The ambient air quality for a given control district depends on: (1) the amount and type of pollutants emitted from the combinations of emission sources, and (2) the prevailing meteorological conditions, topography, and geography. Since the latter vary, sometimes considerably, from one district to another, the restrictions to be placed on the pollutant-emitting industries should also vary to attain the desired ambient air quality without being unnecessarily restrictive. It is also apparent that, for a given set of meteorological conditions, increasingly more restrictive controls would be required on each source as: (1) the number of sources increase, (2) the number and quantity of reactive-pollutant emissions increase.

Many states, counties and cities have their own air-pollution laws in addition to the recent Federal regulations. These local regulations vary to meet the local requirements, although many are patterned after those of Los Angeles County and San Francisco Bay Area. Any person with a pollution problem should check the local regulations first.

Of specific interest in the control of pollutants from small emission sources are Rule 66 of Los Angeles County and Regulation 3 of San Francisco Bay Area. These two rules or regulations are similar to each other and are concerned with control of solvent emissions to reduce smog, which is a particularly difficult-to-correct problem in these two control districts. However, the smog problem is already present in most high population-density areas; hence, the essence of Rule 66 and Regulation 3 is applicable elsewhere.

To indicate the general context that regulations in general may have, pertinent portions of Rule 66 are quoted below as taken from Rules and Regulations, Los Angeles County Air Pollution Control District, June 18, 1970.

Rule 66a - A person shall not discharge more than 15 pounds of organic materials into the atmosphere in any one day from any article, machine, equipment or other contrivance in which any organic solvent or any material containing organic solvent comes into contact with flame or is baked, heat-cured or heat-polymerized, in the presence of oxygen, unless all organic materials discharged from such article, machine, equipment or other contrivance have been reduced either by at least 85 per cent overall or to not more than 15 pounds in any one day.

Rule 66b - A person shall not discharge more than 40 pounds of organic material into the atmosphere in any one day from any article, machine, equipment or other contrivance used under conditions other than described in section (a), for employing, applying, evaporating or drying any photochemically reactive solvent, as defined in section (k), or material containing such solvent, unless all organic materials discharged from such article, machine, equipment or other contrivance have been reduced either by at least 85 percent overall or to not more than 40 pounds in any one day.

Rule 66k - For the purposes of this rule, a photochemically reactive solvent is any solvent with an aggregate of more than 20 percent of its total volume composed of the chemical compounds classified below or which exceeds any of the following individual percentage composition limitations, referred to the total volume of solvent:

1. A combination of hydrocarbons, alcohols, aldehydes, esters, ethers or ketones having an olefinic or cyclo-olefinic type of unsaturation: 5 per cent;
2. A combination of aromatic compounds with eight or more carbon atoms to the molecule except ethylbenzene: 8 per cent;
3. A combination of ethylbenzene, ketones having branched hydrocarbon structures, trichloroethylene or toluene: 20 per cent.

Whenever any organic solvent or any constituent of an organic solvent may be classified from its chemical structure into more than one of the above groups of organic compounds, it shall be considered as a member of the most reactive chemical group, that is, that group having the least allowable per cent of the total volume of solvents.

Regulation 3 does not include trichloroethylene or ketones having branched hydrocarbon structures.

3. Research and Development Recommendations

Introduction

Under the provisions of Section 103 of the Clean Air Act of 1970, the Environmental Protection Agency is required to establish a national research and development program for the prevention and control of air pollution. As part of such a program they shall "conduct, and promote the coordination and acceleration of, research, investigations, experiments, training, demonstrations, surveys and studies relating to the causes, effects, extent, prevention and control of air pollution". The achievement of these broad requirements dictates that survey studies such as this package sorption device study provide problem-solving research and development programs to aid in future planning for governmental action.

A research and development program has been developed based on the results of a thorough review and evaluation of the sources and emissions, as discussed in Chapter 1 of Part I, and control technology relevant to application of package sorption devices, as discussed in Chapters 4 and 6 in Part II of this report. Assessment of these results in terms of present and future technology needs, priorities, and costs has resulted in the formulation of specific and relevant research and development recommendations.

Sources and Emissions

The results of the review of sources emitting noxious, toxic or smog forming pollutants in the range of flow rates amenable to control by package devices showed that the majority of significant emission sources could be assigned to one of two broad categories: (1) solvent users and (2) chemical, thermal, or biological processing industries. Data for characterization of the individual sources within these two broad categories are far from complete, but, in terms of those parameters necessary to the selection and design of package control systems, the solvent user sources and emission are better defined and understood than are the sources in the second category.

Specific problem areas within the solvent user category that have been identified are primarily related to those sources which emit dirty, wet, low solvent concentration gas streams, such as paint spray booths, or which emit pollutants resulting from thermal treatment applied at some point in the process.

Most solvent emissions may be readily characterized as to composition by a knowledge of the composition and physical properties of the original solvent or solvent mixture used.

It is primarily when chemical changes occur through thermal processing, such as baking of coatings, printed products, etc, that emission characterization is lacking. The thermal treatment causes partial decomposition of resins, drying oils and also of high boiling solvents to the extent that the effluent emitted can not be predicted or characterized on the basis of raw material input to the process. Such solvent process emissions bear similarities to emissions from sources in the second broad category of chemical or thermal process industries, such as rendering of meat, poultry, and seafood wastes and by-products; canning and other food processing; and coffee roasting. The emissions are undesirable by-products of the process and are complex mixtures which vary widely according to the type and conditions of processing. To make the best choice of type and design of control system to be applied, an analysis of effluent mixture is necessary to determine the molecular weight range of the gaseous components and type of particulates.

Industry Trends

Certain industry trends are also apparent from the review of pollutant sources and emissions. These may be categorized as (1) solvent changes or reformulation, (2) phase-out of traditional processes, and (3) increase in application of control systems.

Solvent usage throughout the country has been markedly affected by the Los Angeles County Rule 66 and its widespread incorporation into other local and regional legislation. The result is a growing trend toward decreasing or eliminating the active photochemical smog precursors from all types of solvent usage. New, low reactivity solvent mixtures have been developed which simulate the desirable solvent properties of previous reactive systems. Branched aromatics and unsaturates are being eliminated or replaced. Where feasible, water base coatings are substituted for solvent systems. New coatings and printing processes are being developed around solventless systems and nonthermal curing operations.

The indictment against trichloroethene as a smog precursor has resulted in widespread use of alternative degreasing and metal cleaning solvents, particularly inhibited 1,1,1-trichloroethane. The expense and difficulty in controlling degreasing emissions and the availability of substitute solvents will shortly result in the complete elimination of trichloroethene as a vapor degreasing solvent.

Certain traditional processes and industries are being phased-out or are undergoing significant process modifications. Notable among these are the widespread elimination of open burning or backyard incineration of wastes, the replacement of meat smokehouses by chemical treatments, and reduction of leather tanning.

Many metropolitan areas have put into effect bans or limitations on open burning of household, municipal and industrial wastes, with significant reductions of total emissions of organic pollutants. These small sources are not amenable to control and thus complete elimination with substitution of alternative waste disposal methods is the only real solution.

The impact of the accelerating trend toward implementation of existing control technology is difficult to assess in quantitative terms, particularly as it relates to the small emission sources. Some indication may be derived from the organic emission reduction from all stationary sources achieved by the stringent controls in effect in the major metropolitan areas of California. According to the 1969 inventory of emissions for the San Francisco Bay Area, the organic emissions from stationary sources were only about 47 percent of the potential or uncontrolled emissions. Since many of the organic emission sources under control are within the purview of this small source study, it may be seen that implementation of existing control technology can effect significant reduction in emissions.

The proposed R&D programs are so oriented that they do not cover pollution problems that are being corrected by forces or trends already in effect.

Carbon Resorb Systems, Present Technology

The results of the review and evaluation of existing commerically available package sorption devices for control of emissions from small sources show that for the areas of air purification (pollutant concentrations of about 1 ppm and lower) and solvent recovery (recoverable solvent concentration above about 700 ppm), existing control technology is generally adequate and control devices are available. Of the devices used in these two areas, the technology which forms the basis for the solvent recovery type systems is more amenable to general gaseous air pollution control than the air purification technology. In order to apply the solvent recovery type systems to the broader application of air pollution control, modifications are required to the systems and to their operation. To indicate the broader application, these type systems are referred to in this report as the carbon resorb systems.

The carbon resorb systems operate on a cyclic pattern consisting of an adsorption phase and regeneration phase. During the adsorption phase the gas stream, containing the pollutant or solvent vapor, is passed through the (granular) activated carbon bed, usually, until some small amount of the vapors start to penetrate the bed. The gas flow is then stopped or diverted to another previously regenerated bed. During regeneration, a gaseous regenerating agent at elevated temperature is passed through the bed to desorb the pollutant or solvent and restore the carbon to its previous capacity and permit its reuse in the system.

In solvent recovery operations, low temperature steam is used as regenerating agent because of several desirable properties. During regeneration a portion of the steam condenses in the carbon bed and releases considerable heat at 212°F, a temperature at which a great majority of pollutants of interest desorb readily and a temperature which causes very little or no damage to the desorbing vapor or the carbon. The steam and solvent, being condensable, can be readily separated from each other by decantation or distillation.

Carbon resorb systems can be classified into three types depending on the manner in which the carbon bed is handled during adsorption and regeneration. The most commonly used system utilizes two fixed beds which are alternated between the adsorption and regeneration phases of the cycle. The dual fixed bed systems are the simplest of the systems but are also the bulkiest. The other two systems, the moving bed and fluidized bed, move the carbon countercurrent to the gas phases in both the adsorption and desorption phases of the cycle. The countercurrent flows increase the carbon and steam usage efficiency, resulting in operating cost reductions. The disadvantages are the more complex and more costly construction costs of the moving bed type systems and the carbon attrition losses in the fluidized bed systems.

Carbon resorb systems have been used in solvent recovery under conditions which are favorable for profitable recovery of the solvent. Conditions considered favorable are: (1) clean airstream devoid of particulates or containing particulates that are easily filtered out, (2) virtually no vapors in the airstream other than that of the solvent being recovered, (3) airstream at low temperature (130°F or lower), (4) low relative humidity (below 80%) and (5) (most important) vapor concentration over 700 ppm but not over 25% of lower explosive limit.

Carbon manufacturers and solvent recovery system design engineers have the technical knowledge to work out problems associated with recovery of solvents from relatively clean airstreams having high vapor concentrations. Solvent-laden airstreams having these qualities are common in a number of the solvent user industries; namely, degreasing, dry cleaning, most surface coating, flexographic and gravure printing, rubber products and paper coating. The main problem is the coordination of efforts with process machinery designers and plant layout men to attain the best integrated system and thereby the most economical control of air pollution from these emission sources.

Carbon Resorb Systems, New Technology

When conditions and types of pollutant emissions are not applicable to solvent recovery type operations, the situation becomes more complex and, also, competing control systems such as catalytic and thermal incinerators must be brought into consideration. When the pollutant has no recovery value but is combustible and is emitted at concentrations higher than 700 ppm, the incinerator systems are more economical to operate for air pollution control than the carbon resorb systems. For a noncombustible pollutant the control is of course limited to the carbon resorb or absorption type systems. At pollutant concentrations below 700 ppm the new technology on carbon resorb systems is in competitive position with the incinerator systems for pollution control.

At progressively lower concentrations the use of steam as regenerating agent becomes increasingly less suitable while noncondensable inert gas or air at 200° to 300°F, on basis of theory, shows economic advantages. At low concentrations, large amounts of steam are required to maintain a practical operating capacity for the carbon and it becomes impractical to separate the pollutant from the large volume of steam condensate. Use of steam would convert the air pollutants to water pollutants.

With noncondensable gas regeneration, several economically feasible procedures have been worked out on sound engineering principles for the carbon regeneration and separation or disposal of desorbed pollutant vapors. When the pollutant vapor is combustible and has no recovery value, it becomes economical to dispose of it by catalytic or thermal incineration. In this application the incinerator need be about one-tenth of the size that would have been required to incinerate the air initially. If it is necessary or desirable to recover the desorbed pollutant vapor for reuse (solvent) or disposal by other means, it can be done by readsorption on a secondary carbon bed or by condensation.

The secondary adsorber would be small relative to the primary adsorber and could be readily regenerated by the conventional steam method. When the pollutant vapor is readily condensable, it can be partially condensed from the hot regenerating gas by cooling, with the cool regenerating gas being recycled through the (other) on-stream carbon bed. These conceptual designs can be incorporated into the fixed bed, moving bed or fluidized bed carbon resorb systems.

Economic analyses show that the various above proposed carbon resorb systems are definitely more economical to operate than catalytic or thermal incinerators of equivalent air handling capacities for air at near 77°F initial temperature. At elevated airstream temperatures the incinerators become increasingly more economical to operate and could equal the carbon resorb systems in operating costs. There is therefore a definite area in the air pollution control scheme where the new carbon resorb systems technology should be seriously considered.

Adsorption Theories

Two theories related to adsorption dynamics have been advanced which can greatly facilitate development of the carbon resorb systems new technology for pollution control. (Chapter 4)

One of these is the Polyani potential theory which can be used to calculate the adsorptive capacities of carbons for various homologous series of molecules as function of temperature, molecular size and concentration.

The other theory involves mass transfer of vapor from the airstream to carbon and into the pores of the carbon. On the basis of mass transfer theories Klotz developed an equation which can be used to calculate the mass transfer zone or adsorption zone length in the bed. The controlling parameters are: air density and viscosity, carbon particle size, airflow velocity, diffusion coefficient of vapor in air, and ratio of vapor influent concentration over vapor concentration within the bed.

The effective use of either equation requires minimal data on adsorptive capacities and adsorption rates on the particular carbon and homologous series of the pollutant or pollutants under consideration. Data that would be useful for this purpose, particularly from the problem areas of pollution control, are lacking or are not in a form suitable for use by the engineer that would do the development and/or design of the control system.

Monitoring Instruments

In solvent recovery operations the instrumentation requirements for monitoring are not complex. The solvent, the rate of emission, and concentration are known to a fair degree of certainty permitting the installation of optimum size and design of carbon resorb system for the particular emission source. The adsorption-regeneration cycles are preset and automatically controlled at short and equal time intervals. A comparison of solvent recovery with the solvent input will give a measure of the efficiency of the recovery operations. Simple instruments such as a manometer and temperature recorders are used to determine the time for particulate filter change and to check the air inlet temperature and temperature profiles during adsorption and regeneration.

In the problem areas of pollutant control, the emissions can be quite variable in quantity and type. The adsorption phase time can therefore vary considerably. Monitoring instruments are highly desirable to avoid overrun or large underrun on the adsorption phase. The instruments for this purpose should be simple and durable in construction, low cost, and readily understood and operated by plant operating personnel.

Chapter 8 describes techniques and instruments that show suitability for monitoring of pollutant vapor concentrations. Some have capabilities for identifying pollutant vapors. Much of the available instrumentation are too expensive and also require technically trained personnel for their operation.

Research and Development Programs

Specific programs resulting from the identification of needs and priorities are described below. Study priority is based on three relative classifications: high; medium; low. Estimated cost is based on a nominal $50,000 per man-year unless unusually high materials or construction costs are involved. For the latter cases, estimated costs of such materials or construction are added.

The recommended programs are divided into four areas of study:

Emission and Source Characterization
Evaluation of New Adsorbent Systems
Generation of Adsorption and Regeneration Data
Monitoring Instrument Development

Emission and Source Characterization

Objective - To provide detailed chemical and engineering data necessary for the selection and design of optimally effective control systems.

Approach - Pollutant sources recognized as being particularly difficult to control due to low (below 700 ppm range) pollutant concentration, highly odorous nature, presence of aerosols or particulates, and presence of difficultly adsorbed species would be investigated in detail. Specific tasks would include problem emission source selections, field testing of emissions, engineering evaluation of overall process with determination of process flows and point sources, and process modification required to make the most effective use of a potential control system.

The data obtained on some sources may clearly define the best choice of system, i.e., catalytic incineration, thermal incineration, liquid absorption, or carbon resorb. Further study to determine the best suited type and optimum size of system may be minimal and done with readily available information. It is foreseeable that commercially available carbon resorb systems may be suitable for some applications. If the emission and source characterization data do not indicate a clear choice of competing system and also leaves best choice of carbon resorb system in doubt, further investigation as prescribed under the program to Evaluate New Adsorbent Systems is required.

Priority, Duration, Effort and Cost - This program was assigned a high priority rating since characterization of the emission source is absolutely essential before a logical procedure can be planned for its control.

The number of point sources of emissions is large with new ones appearing as new products and processes are developed and old ones phased out as they become obsolete. It is foreseeable that many sources will be quite similar, and the characterization of one will essentially characterize the others. This pattern will reduce the number of investigations that need to be made to a limited number of the more critical ones. It is difficult to assess with any certainty the number of critical sources existing. The difficulty of characterization also varies, but with a well equipped laboratory and trained personnel the cost per source can vary from $5,000 to $15,000 each. The characterization would be carried only to the degree required for control system selection and to establish design, size, and operating procedure. It is quite certain that a minimum of 10 sources would require characterization and it appears improbable that the number would rise much above 30.

Ten sources would require about 3,800 man hours at a cost of $100,000 to be performed in less than one year.

A more extended program of systematic characterizations and including possible new sources would increase cost and time. At some point in time the need for further studies would diminish and if 30 sources is arbitrarily set as maximum the man hour requirement would be 11,400 to be performed over a five year period at a cost of $300,000.

Evaluation of New Carbon Resorb System

Objective - To evaluate, technically and economically, potentially promising or incompletely proven carbon resorb systems and to demonstrate feasibility of the selected system for control of pollutants emitted from specific sources of the type studied under Emissions and Source Characterization.

Approach - On the basis of data obtained from the Emission and Source Characterization study or from other sources, the first step of the program would be to determine whether a carbon resorb system should be used, and, if so, which type. Systems that are of foreseeable interest are briefly described as follows:

Dual stationary beds for adsorption phase, regeneration with hot noncondensable gas, and disposal of desorbed vapors by catalytic or thermal incineration.

Dual stationary beds for adsorption phase, regeneration with hot noncondensable gas, readsorption of desorbed vapors in small secondary adsorbed and ultimate recovery of vapors by conventional steam regeneration.

Dual stationary beds for adsorption phase, regeneration with hot noncondensable gas, recovery of vapors from regeneration gas by condensation.

Alternatives for each of the above three systems would be the use of moving carbon bed or fluidized carbon bed.

Polar adsorbent systems (for low molecular weight polar vapor).

In order to make the choice of system, some fundamental adsorption studies may be required (laboratory scale) to obtain additional data for the calculation of adsorptive capacities, adsorption zone lengths, carbon bed sizes, service times, regenerability, and regeneration gas requirements. On the basis of all of the acquired information, several models of carbon resorb systems would be designed that appear technically and economically attractive. From the theoretical performance of the best model, when compared to performances of incinerators, a decision is then made whether to continue further to demonstrate feasibility of the system under test conditions.

If a system demonstration is indicated, the second step would be the construction or assembly of a pilot sized system, which would be tested in the contractors pilot plant or under actual conditions in industry. The choice of location would be determined by several factors. If the operating conditions can be reproduced in a pilot plant, the pilot plant would be the preferred location since the tests can be better controlled to yield data that can be treated theoretically. Spray painting operations would be an example of this type. A pilot plant location would be preferred when the study involves vapors in the explosive concentration range, as would be the case of emissions from gasoline storage. When the vapor emission conditions cannot be reproduced in the pilot plant, as would the case with pollutants emitted from a rendering plant, the preferred location is the plant of the industry emitting the pollutant.

Priority, Duration, Effort and Cost - This program was assigned a high priority rating since it involves the basic objectives of the package sorption study.

About 5,000 man hours over a one year operating time would be required to test a control system. The estimated cost would vary between \$135,000 and \$145,000 when equipment costs vary between \$10,000 and \$20,000. Equipment costs at this level would limit test control systems to airflow capacities of less than 2,000 ft^3/min.

The size of the program depends on the number of system tests that are deemed necessary to get adequate information on feasibility of carbon resorb type systems for pollution control. Four industries that should receive top priority for control study are: meat rendering, fish rendering, spray coating and petroleum distillate evaporation. For a limited study (million dollar total program level), these four should receive first consideration. It may become necessary to test more than one design of carbon resorb system at each of the emission sites, in which case more than four systems would be tested. For a four system study at $140,000 each, the total cost would be $560,000. The systems can be tested simultaneously or extended over four years.

Depending on the results of the first four systems studied, the program may be discontinued or extended to include other emission sources such as waste water treatment, soap manufacture, restaurants, baking, plywood manufacture, azo-dye manufacture, crematoria, hospital exhausts, etc. The program will ultimately reach a point of diminishing returns where the results of previous tests are translatable to new situations and no further testing is economically justifiable. The point at which further testing is not justifiable is difficult to determine, but it is believed that at the level where control systems for 12 or 13 emission sources of varied types have been tested the point of diminishing returns has been reached.

For 13 systems at $140,000 each, the total cost would be $1,820,000.

Generation of Adsorption and Regeneration Data

Objectives - To generate adsorption and regeneration data in forms readily usable by the carbon resorb systems design engineer.

Approach - The recommended research program to obtain and compile these data would consist of laboratory scale studies conducted under gas flow rates of the order of 0.1 to 0.4 cubic feet per minute and carbon bed diameters of one-half to one inch. These conditions are sufficient to give the necessary data without excessive expenditures in time or equipment.

Due to the large number of pertinent parameters and their permutations to be investigated in this proposed program, careful utilization of statistical experimental design procedures would be employed. The pertinent variables and suggested levels of experimentation for each variable are shown below:

Variable	Levels
Carbon type	2 - significantly different pore structures (source of carbon)

Variable	Levels
Pollutant type	3 levels for each homologous series or chemical group classification of interest
Pollutant concentration	3 - 10, 100 and 1000 ppm
Gas velocity	3 - 20, 60 and 100 ft/min
Bed depth	3 - longer than adsorption zone
Mesh size	3 - 4 to 6, 6 to 10 and 10 to 30 mesh
Temperature	3 - 25°, 50° and 100°C
Humidity	Spot checked only, little expected effect

Regeneration runs with a noncondensable gas (nitrogen) would be conducted at two temperatures on carbon beds spent with various pollutants at the varied concentrations as indicated above. Also repeated cycles will be carried out. About forty regenerations are foreseeable.

The product of the study would be tables, graphs, equations and procedures for calculating adsorptive capacities, operating capacities, adsorption zone lengths, and regenerating agent requirements. These results would be further utilized for estimating carbon bed dimensions, service time, adsorption-regeneration cycle timing and frequency and for determining effective disposal techniques for the pollutant.

Priority, Duration, Effort and Cost - This program was assigned a medium priority rating since the information it would yield would be used primarily to expedite the progress in the program to Evaluate New Carbon Resorb Systems. In the latter program adsorption and regeneration data, if required, would be experimentally determined specifically for each pollutant emission source. This procedure would be less efficient, more costly, and produce information that would be limited in regard to general application than if a systematic study were conducted as proposed here.

To attain a fairly complete coverage of parameters, homologous series of compounds, and carbons, the program would require 15,200 man hours of effort over a 3-yr period. Considerable instrumentation is required since some adsorption phases of the experiments would be run continuously over extended periods with continuous monitoring of the effluent gas stream. The instrument and other equipment costs come to $20,000. The total cost would be $400,000.

Some phases of the program are more important than others and the study of some homologous series of compounds are more pertinent to problem areas in pollutant control than others. On the basis of priorities in this respect, the three year overall program can be divided into three one-year programs. The first year's program, however, would be the least productive since it includes a considerable lag time for the purchase and installation of the instruments, adsorption and regeneration systems. It includes 16 weeks equipment installation period followed by 36 weeks of experimental work and final report preparation. The man hours would be 4,500 at a cost of $130,000, including the $20,000 for instruments and equipment. A two-year program would be an expansion of the one-year program with considerably larger portion of the estimated 9,800 man hours assigned to experimental work. The cost, including instruments and other equipment, would be $265,000.

Monitoring Instrument Development

Objective - To develop effective and relatively inexpensive methods for monitoring the operation of package sorbent devices.

Approach - Three promising areas of monitoring instrumentation research and development have been preliminarily explored and recommended for further study. These are:

1. Indicator Tubes - Development of chemical indicator methods for detecting breakthrough or monitoring of service life of carbon sorption systems. This area of research and development would rely heavily on the extensive work already done in the development and application of selective and specific indicator tubes for a wide variety of both organic and inorganic air contaminants.

2. Sorption and Incineration Devices - Development of monitoring devices applicable to organic contaminant control by either carbon sorption or incineration systems, based on the principle of the catalytic CO indicator, widely used in vehicular tunnels and other areas having significant potential for hazardous CO concentration build-up. The

catalyst used in these indicators, Hopcalite, is an effective oxidation catalyst for not only CO but hydrocarbons. Thus, the presence of hydrocarbons in the control system exhaust could be detected by a temperature increase of an adiabatically operated Hopcalite catalyst bed. A steadily increasing temperature difference between the Hopcalite bed and the effluent airstream would indicate pollutant penetration.

3. Stack-Gas Samplers - Development of a simple stack sampling device by which, periodically, the control device users could collect samples to be quantitatively analyzed at a centrally located analytical laboratory. Such a device could be similar to those used by industrial hygienists in collecting work room air samples for subsequent analysis, which use a small carbon canister and hand pump to collect and retain air contaminants. Alternately, such sampling canisters could be integrally installed as part of the control system and would be periodically removed and sent for analysis.

Priority, Duration, Effort and Cost - This program was assigned a medium priority since the need for the relatively inexpensive monitoring methods would not arise until operational control systems have been developed, i.e., results of the program to Evaluate New Carbon Resorb Systems.

This study is expected to require 12,500 man hours over a 2-yr period at a cost of $375,000.

Summary

The contract specified the development of two 5-year programs, Plan A and Plan B, based on assumed total expenditures of $1 million and $5 million, respectively. The various programs as described above have been grouped into Plan A of $1 million total expenditure and Plan B of $3 million total expenditure as shown in Tables 3-I and -II, respectively. An expanded plan of $5 million was not foreseen.

Table 3-I Summary of One Million Dollar Research and Development Plan (A)

Program	Cost, $	Time schedule, yr 1	2	3	4	5	Priority
Emissions and Sources Characterization (30 sources at $10,000 each)	300,000	—	—	—	—	→	high
Evaluation of New Adsorbent Systems (4 systems at $140,000 each)	560,000	—	—	—	→		high
Generation of Adsorption and Regeneration Data	130,000	→					medium
Total	990,000						

Table 3-II Summary of Three Million Dollar Research and Development Plan (B)

Program	Cost	Time schedule, yr					Priority
	$	1	2	3	4	5	
Emissions and Sources Characterization (30 sources at $10,000 each)	300,000	—	—	—	—	→	high
Evaluation of New Adsorbent Systems (13 systems at about $140,000 each)	1,820,000	—	—	—	—	→	high
Generation of Adsorption and Regeneration Data	400,000	—	—	—	—	→	medium
Monitoring Instrument Development	375,000	—	→				medium
Total	2,895,000						

Part II

Package Sorption Device Technology Handbook

Introduction to Part II

This part of the report presents the results of the investigations and analyses of the packaged systems that are or could be used for control of air pollutants from those emission sources discussed in Chapters 1 and 2. Although this study was primarily concerned with sorbent systems, the competing systems - catalytic and thermal incinerators - are also discussed in order to place each system in proper perspective in regard to its effectiveness and operating cost.

Chapter 6, Package Sorption Systems, is the most important chapter of Part II. In it are discussed (1) the present sorbent systems technology, (2) the new developments and proposed systems that show promise for pollutant control and (3) the operating costs of the various systems. Under present systems technology, systems are considered that are in wide commercial usage or have been proven over a number of years of successful operation. Under new technology, systems are considered that have appeared very recently in commercial usage but have not yet acquired wide spread acceptance or systems that have been engineered on theoretical basis but have not been tested or tested on a very limited pilot plant scale.

Since one of the important objectives of the study was to assess potential new technology to control pollution, Chapter 6 was written against a theoretical background. A theoretical understanding of the adsorption and regeneration processes permits a ready extension of the operational knowledge on known systems toward the design of new systems for control of pollutants emitted under new and more difficult circumstances. Chapter 4 was written to supply this information in considerable detail. Chapter 5 is a considerably more condensed review of catalytic combustion theory.

Chapter 7 presents a brief study of catalytic incineration to augment the more extensive study of sorbent systems.

When the new systems become commercial, the need for new testing and control instrumentation is foreseeable. Chapter 8 describes basic concepts suitable for pollutant identification and concentration measurements.

4. Sorbent Types and Sorption Theories

Sorbent Types

Important Sorbent Properties

Sorbents differ considerably from each other in their selectivity, or preferential adsorption, and their adsorptive capacities. These two factors can vary the suitability of a sorbent for air pollution control usage, limiting some for special conditions, while others are generally applicable. The selectivity and capacity are dependent on four properties of the sorbent. These are:

1. Chemical constitution of the sorbent, particularly the surface,
2. Extent of the surface area,
3. Pore size distribution,
4. Particle, or granule, size.

The term "sorbent" includes two types of solids (1) those that concentrate vapors on the free surface by "adsorption", and (2) those that concentrate vapors by "absorption", wherein the vapor molecules penetrate into the mass of the sorbent solid. Penetration of hydrogen into palladium metal lattice is an example of the latter. At present, the absorption process in solids (to differentiate it from liquid absorption) does not appear to play any role in the control of pollutant emissions of the type discussed in Chapters 1 and 2.

On the basis of chemical constitution and pore size distribution, adsorbents can be grouped into four different types. They exhibit greatly different selectivities for vapors and differences in manner of adsorption. The types are:

1. Chemically reactive adsorbents,
2. Polar adsorbents,
3. Nonpolar adsorbents,
4. Molecular sieves.

The differences in adsorptive behavior of the first three are primarily due to differences in chemical constitution of the solids, with secondary differences contributed by extent of surface area and pore-size distribution. The molecular sieves can be either polar or nonpolar, but their distinctive adsorptive behavior is due to the small size of the pores which physically block entry of oversized molecules.

Chemically Reactive Adsorbents

When adsorption of vapors is accompanied by a chemical reaction, the process is defined as "chemisorption". It has a number of well defined characteristics which are enumerated below:

1. It is highly selective; not all vapors react with all adsorbents.
2. It tends to be irreversible.
3. The rate increases with rise in temperature.
4. The heat of chemisorption is of the same magnitude as that of chemical reactions, usually over 10 kcal/mole.
5. The process is exothermic.
6. Chemisorption stops when all of the active sites on the surface have reacted, or the surface is covered with a unimolecular layer of chemisorbed vapor.

Examples of chemisorption, which have been intensively studied by various investigators, are hydrogen on heated metals, oxygen on heated tungsten, carbon monoxide on iron catalysts, nitrogen on nickel and iron, and ammonia on alumina (Langmuir, 1912 and 1916; Emmett, 1937; Beeck, 1950; Webb, 1957). Chemisorption of oxygen on carbon is well known. At higher temperatures, it is one of the steps in carbon activation; i.e., H_2O vapor and CO_2 react with carbon to form an oxygen surface complex which later breaks up by releasing CO.

Inorganic acid vapors react readily with transition metal oxides. When the active metal oxides are used to catalyze pollutant incineration, chemisorption of acid vapors plays an adverse role by causing catalyst poisoning. Conversely, chemisorption on reactive metals is a potential process for purifying air of traces of halogen acids and SO_2.

Soda lime by itself, or in combination with activated carbon is used to chemisorb vapors such as ethanoic acid, ethanenitrile, propenenitrile, 3-chloro-propene, ethenyl propyl disulfide, chlorine, cyanogen, fluorine, hydrogen bromide, hydrogen chloride, hydrogen fluoride, and hydrogen sulfide. Several of these vapors have been identified with the rubber products and rendering industries.

In the chemically reactive adsorbent group are also the impregnated polar and nonpolar adsorbents wherein the impregnant reacts chemically with the vapor molecule after an initial physical adsorption has occurred. Table 4-I listed impregnant-adsorbent combinations and the vapor molecules to which the impregnant is reactive.

Table 4-I Types of Impregnated Adsorbents

Impregnant-adsorbent	Pollutant vapor
Bromine-carbon	ethene
Iodine-carbon	mercury, radioact. iodine
Phosphoric acid-carbon	ammonia
Potassium permanganate-activated alumina (Purafil)(1)	low molecular wt mercaptans, organic acids olefins
Cupric oxide-carbon	carbonyl chloride (phosgene)
Cupric oxide-pentavalent chromium on carbon	cyanogen chloride hydrogen cyanide carbonyl chloride
G-32E-treated activated carbon(2)	sulfur compounds hydrogen sulfide carbonyl sulfide mercaptans from hydrocarbon gases
Ammonia-molecular sieves	carbon dioxide hydrogen sulfide mercaptans carbon disulfide
Copper-activated alumina (8.4 wt %)	sulfur dioxide
Sulfur acid-carbon (20 wt %)	thiophenol and similar compounds

(1) Marbon Chemical Division, Washington, West Virginia
(2) Chemetron Corporation, Catalyst Division, Louisville, Kentucky

Polar Adsorbents

When adsorption is not accompanied by chemical bonding, the active forces are referred to as van der Waal's forces and are the same as those that bind liquids and solids. This type of adsorption is also referred to as physical adsorption and occurs on chemically nonreactive adsorbents having polar or nonpolar surface properties.

Physical adsorption varies from chemisorption in several respects in that:

1. It is less selective.
2. It is reversible.
3. The heat of adsorption is of the order of 10 kcal/mole.
4. Adsorption can continue beyond the unimolecular layer surface coverage.
5. The amount adsorbed decreases with increasing temperature at a fixed vapor pressure.

Examples of polar adsorbents are silica gel, activated alumina, fullers earth, bentonite, and the zeolite type of molecular sieves. Of these, fullers earth and bentonite are usually used for liquid phase adsorption processes; the other three are used in gas separation and purification processes.

The chemical make-up of these adsorbents consists of silicon oxide and/or aluminum oxide groupings which impart a highly polar character to the surface. Silica gel is essentially pure SiO_2 with less than 0.3% of other metallic oxide impurities. Activated alumina is over 98% pure Al_2O_3 with other metallic oxides as impurities making up the balance. Zeolites are alumino-silicate crystalline structures containing sodium, potassium or calcium cations.

The polarity of the surface has been found to produce strong affinity to polar vapor molecules or vapor molecules that are readily polarized, such as olefins. Table 4-II lists a number of air pollutants in decreasing order of affinity on silica gel (Trappe, 1940) which shows the effect of physical properties of the pollutants, particularly the dielectric constant and dipole moment, on the adsorption affinity. Except for a few variances, the affinity decreases with decreasing dielectric constant and decreasing dipole moment. In contrast, the affinity tends to decrease with increasing V_m and van der Waals' constant $\underline{a}$; for definition of van der Waals' $\underline{a}$, see Appendix D. The latter trend

Table 4-II Effect of Pollutant Physical Properties on Adsorptive Affinity for Silica Gel, Decreasing Order of Affinity Downward

Pollutant	Dielectric constant at 67°F	Dipole moment $\times 10^{18}$ esu	V_m, cm^3/mol	van der Waals' $a \times 10^3$
Water	81.0	1.85	18	11
Methanol	31.2	1.73	42	19
Ethanol	25.8	1.70	61	24
1-Propanol	22.2	1.65	84	30
Propanone	21.5	2.89	74	28
Ethyl acetate	6.1	1.74	106	41
Ethyl ether	4.4	1.15	106	35
Trichloromethane	5.2	1.02	83	30
Dichloromethane	9.1	1.54	65	
Benzene	2.3	0.00	95	36
Toluene	2.3	0.36	118	48
Tetrachloromethane	2.2	0.00	101	40
Cyclohexane	2.0	0.2	118	43
Hexane	1.9	0.00	140	49

contradicts the concept of active van der Waals' forces when dealing with polar adsorbents. Adsorptive affinity on non-polar adsorbents correlate with van der Waals' a, as will be shown in the next section.

The strong affinity of polar adsorbents for water greatly limits their general use in air pollution control. They are used for drying of various gases; some are listed below:

Ammonia
Argon
Butane
Carbon dioxide
Chlorine
Ethane
Ethene
Freons
Helium
Hydrogen
Hydrogen chloride
Hydrogen sulfide
Methane
Nitrogen
Oxygen
Propane
Propene
Sulfur dioxide

When the gas stream is free of water vapor, polar adsorbents are suitable for pollution control involving small polar molecules such as:

Ammonia
Dichloromethane
Hydrogen chloride
Methanal
Methanol
Sulfur dioxide
Hydrogen sulfide

In each case the pollutant can be desorbed with a relatively small amount of water, after which the polar adsorbent can be dried at elevated temperature and put back into use.

Nonpolar Adsorbents

Activated carbon is the primary example of a nonpolar adsorbent. Others are possible such as metallic surfaces, but the surface areas attainable with the latter are too small to be useful for gas or air purification.

Physical adsorption on nonpolar and polar adsorbents differ primarily in selectivity, or differences in affinity, for different molecules. On nonpolar adsorbents adsorptive affinity increases with molecular size and van der Waals' constant a. In Table 4-III this is shown with seven hydrocarbons, which are listed downward in increasing order of adsorptive affinity on activated carbon (based on data of Ray, 1949). The correlation of V_m with amount adsorbed has been worked in with the Polanyi potential theory to derive an equation for calculating the amount of adsorption of various pollutants at varied vapor pressures and temperatures. This equation is discussed under the theoretical part of this chapter.

By impregnating activated carbons, polar adsorbent and chemically active adsorbent properties can be imparted to them. Activated carbons generally contain ash, such as SiO_2, Al_2O_3, Fe_2O_3, NaOH, KOH and chemisorbed oxygen, all of which

Table 4-III Effect of Pollutant Physical Properties on Adsorptive Affinity for Activated Carbon at 100°F, Increasing Order of Affinity Downward

Pollutant	Amount adsorbed at one atmosphere pressure, cm^3 liq./g	V_m, cm^3 liq./mol	van der Waals a x 10^3
Methane	0.03	30	4.5
Ethyne	0.11	37	8.7
Ethene	0.14	44	8.9
Ethane	0.20	52	10.7
Propene	0.31	67	16.7
Propane	0.36	74	17.3
Butane	0.43	96	28.8

impart polar properties. By leaching out the ash followed by hydrogen reduction, a wholly nonpolar carbon can be obtained. Adsorption of water vapor at low vapor pressures is very sensitive to the presence of polar impurities. Activated carbons that have not been specially treated are poor adsorbents for water and can be desorbed by most of the organic pollutants emitted from the small sources.

Molecular Sieves

Molecular sieves are available having polar or nonpolar surface properties. The polar molecular sieves are complex crystalline structures consisting of basic units or tetrahedra of $(Al, Si)O_4$. The silicon atom is electrically balanced by the four oxygen atoms of the lattice, but the aluminum atom, with a valence of three, is not. For every aluminum atom in the lattice, a monovalent (or equivalent) cation is required to attain electrical balance. The cations used are Na, K, and Ca.

When first manufactured, the crystalline structure contains water of crystallization, which is removed by heating to temperatures above 570°F. The removal of the water leaves a porous solid consisting of a network of cavities interconnected by round pores of smaller diameter. The cavity and pore diameters are uniform; hence, a pore-size distribution in the usual sense as applied to silica gel, activated alumina and activated carbon has no significance in molecular sieves.

The manufacturers of polar molecular sieves (Linde, Davison) designate over four different types of sieves. A group A has 11.4 Å cavity diameter, a 1 to 1 Al to Si ratio and is designated as simple cubic crystalline structure. A group X has a 1.0 to 1.25 or 1.5 Al to Si ratio and is designated as body-centered cubic crystalline structure. By changes in Al to Si ratio and type of cation, the pore diameter can be varied over the increments 3, 4, 5, 8 and 9 Å. In each case only molecules having critical dimensions smaller than the nominal pore size can be adsorbed. Table 4-IV lists the types of Linde molecular sieves and their general chemical formulas; those of Davison are quite similar. Table 4-V also gives the nominal pore diameters and lists some of the pollutants that can be selectively adsorbed by each type of molecular sieve, as determined by the critical dimensions of the molecule. For a given molecular sieve, those molecules listed under sieves of larger pore diameter are screened or sieved out while those listed under sieves of smaller pore diameter are adsorbed.

Table 4-IV Types of Molecular Sieves

Type	General formula, molar ratios
3A	$0.72\ Na_2O : 0.24\ K_2O : 1.00\ Al_2O_3 : 1.92\ SiO_2 : 2H_2O$
4A	$0.96 \pm 0.04 Na_2O : 1.00\ Al_2O_3 : 1.92 \pm 0.09\ SiO_2 : xH_2O$
5A	$0.72\ Na_2O : 0.24\ CaO : 1.00\ Al_2O_3 : 1.92\ SiO : 2H_2O$
10X	$0.62\ N_2O : 0.21\ CaO : 1.00\ Al_2O_3 : 2.48\ SiO_2 : xH_2O$
13X	$0.83 \pm 0.05 Na_2O : 1.00\ Al_2O_3 : 2.48 \pm 0.03\ SiO_2 : xH_2O$

Superimposed on the sieving action of these adsorbents is the strong affinity for small or highly polar molecules; see discussion under Polar Adsorbents. As was the case with silica gel and activated alumina, the strong affinity of molecular sieves for water greatly limits their uses for pollution control. In a dry airstream, the molecular sieves are more effective for the adsorption of low molecular weight polar or unsaturated pollutants at low concentrations than silica gel, activated alumina or activated carbon. Results presented below, as reported by Gustafson (1961), show this difference in the adsorption of ethene and ethyne at 77°F and 20 mm of Hg pressure.

	Amount adsorbed, % by weight		
Gas	4A	silica gel	activated carbon
Ethene	6	1.75	2.5
Ethyne	7	1.5	1.8

The adsorption of low molecular weight saturated hydrocarbons such as methane and ethane are more strongly adsorbed by carbons than by molecular sieves, but too poorly in any case to be used effectively in pollution control. Activated carbons will have a much lower equilibrium capacity for organic compounds at low partial pressures than 13X; but at high partial pressures, activated carbon adsorptive capacity is two to three times that of 13X. Molecular sieves adsorb NO_x gases at high relative humidities with about 5 wt % pick-up at concentrations in the 1,000 to 2,000 ppm range (Sundaresan, 1967).

Molecular sieves are readily regenerated by passing water vapor or liquid water through the sieve bed and the adsorbed water, in turn, is readily removed by heating the bed to 570°F.

Table 4-V Effect of Molecular Sieve Pore Diameter on Selective Adsorption of Pollutant Vapors

Sieve type and pore diameter, Å	Pollutant	Critical diameter of pollutant molecule, Å
3A 3Å	Ethyne	2.4
	Carbon monoxide	2.8
4A 4Å	Water	3.2
	Ammonia	3.6
	Hydrogen sulfide	3.6
5A 5Å	Ethene	4.2
	Ethane	4.4
	Methanol	4.4
	Ethanol	4.4
	Methanethiol	4.5
	Propane	4.9
10X 8Å & 13X 9Å	Butane to $C_{22}H_{46}$	4.9
	Propene	5.0
	Ethanethiol	5.1
	1-Butene	5.1
	2-Butene	5.1
	1,3-Butadiene	5.2
	Isobutane to iso $C_{22}H_{46}$	5.6
	Cyclohexane	6.1
	Benzene	6.7
	Toluene	6.7
	p-Xylene	6.7
	Tetrachloromethane	6.9
	Trichloromethane	6.9
	m-Xylene	7.1
	o-Xylene	7.4
	Triethylamine	8.4

In recent years (since 1969) developmental work has been done on carbon molecular sieves. Because of nonpolarity of the surface, these adsorbents would have no greater affinity for small polar molecules than for nonpolar molecules. Preferential adsorption for small organic molecules can be expected in the presence of moisture. Pittsburgh Carbon Company, Division of Calgon Corporation, has developed a carbon molecular sieve which shows very little adsorption for tetrachloromethane but considerable adsorption for iodine. The pore openings appear to be slit or rectangular shapes of critical dimension in the 5.0 to 5.5 Å range.

Because of attractive forces from adjacent and opposite pore walls, such pollutants as ammonia, hydrogen sulfide and possibly methanethiol can be expected to be adsorbed more strongly than on conventional carbon. As with polar molecular sieves, the sieving action can be utilized for separation of molecules of differing sizes.

Cooper (1970) describes a platinum-carbon catalyst having molecular-sieve properties. The platinum is incorporated into the carbon structure during the molecular sieve preparation. With these catalytic-carbon sieves, hydrogenation of linear olefins can be carried out because of their penetration into pores while branched olefins are not hydrogenated.

Effect of Physical Properties on Adsorption

Physical Properties - The chemical constitutions of the adsorbents, as discussed in the previous text, form the basis for classifying the adsorbents into three types: the chemically reactive, polar and nonpolar. A fourth type, decided primarily on pore structure, is the molecular sieve which in chemical constitution can also be classified polar or nonpolar.

The physical properties such as surface area, pore size distribution, pore volume, granule or particle size and density determine the adsorptive capacity, adsorption rate and resistance to flow of the pollutant-air mixture through the adsorbent bed. These properties are very frequently presented in sales literature to indicate the quality of the adsorbent being sold. Tables 4-VI and -VII present ranges of most of these physical properties for commercially available silica gels, activated aluminas, activated carbons and molecular sieves. Comparative data for chemically reactive adsorbents were not available and would not have the same significance since chemisorptions are very specific.

To further define the adsorptive qualifications, sales literature presents adsorption isotherms and/or adsorptive capacity data at varied conditions for various vapors for which the adsorbents are recommended. For polar adsorbents and polar molecular sieves, the graphical presentation of the water adsorption isotherm or adsorptive capacities at varied relative vapor pressures are usually the first adsorptive capacity data given. For activated carbons the iodine number is most frequently given if the intended use is in aqueous phase. When the intended use is in gas phase, it is the carbon tetrachloride (tetrachloromethane) activity. The carbon tetrachloride activity is the weight percentage adsorbed at 40°F and 0.16 relative vapor pressure. Details of this test are given in Appendex D.

Table 4-VI Physical Properties of Adsorbents, Surface Areas and Pore Volumes

Adsorbent	Surface area m^2/g	 m^2/cm^3	Pore volume cm^3/g	 cm^3/cm^3
Silica gel	750	520	0.40	0.28
Activated alumina	210 to 360	210 to 320	0.29 to 0.37 est	0.29 to 0.33 est
Activated carbon	600 to 1600	300 to 560	0.80 to 1.20	0.40 to 0.42
Molecular sieve	----	----	0.27 to 0.38	0.22 to 0.30

Table 4-VII Physical Properties of Adsorbents, Densities and Mean Pore Diameters

Adsorbent	Bulk density, g/cm^3	Particle density, g/cm^3	True density, g/cm^3	Mean pore diameter, Å
Silica gel	0.70	1.2	2.20	22
Activated alumina	0.90 to 1.00	1.5 to 1.7 est.	3.30	18 to 20
Activated carbon	0.35 to 0.50	0.60 to 0.80	2.20	15 to 20(1)
Molecular sieve	0.80	1.40	2.3 to 3.3	3 to 9

(1) Carbon pore structure consists of two pore size ranges, (1) those over 30 Å diameter termed macropores, and (2) those less than 30 Å diameter termed micropores. The 15 to 20 Å mean diameters are for the micropores only; 95% of the surface area is associated with them.

Surface Area - In the adsorption process, the pollutant molecules in the gas phase are attracted to the adsorbent surface initiating a unimolecular layer of molecules which can spread until complete surface coverage is achieved. This is definitely the case with chemisorption. When adsorption occurs by van der Waals' forces, multilayers of molecules can form after completion of the unimolecular layer, or sooner if other factors are active. Other factors encountered in porous adsorbents are the attractions of the adjacent and opposite pore walls when pore diameters are small.

The opposite-wall attraction, or effect, enhances the adsorption to the degree that molecular packing can occur in the pores, not unlike capillary condensation. The stage at which molecular packing starts is dependent on (1) relative sizes of the adsorbed molecule and pore diameter, and (2) the mutual attraction of the molecules relative to the attraction of the molecules to the adsorbent surface. When the molecular diameter is larger or mutual attraction is strong, molecular packing starts early in the adsorption process.

The extent of the surface area is then a sole measure of the adsorptive capacity only when the molecule is small, has strong affinity to the adsorbent such as water on polar adsorbents, and the relative vapor pressure is low. At increased relative vapor pressures, multilayer and capillary condensations can still occur. When the mutual attraction is greater than the surface attraction, the molecule is repelled as mercury from carbon. When the mutual attraction is not too greatly different from the surface attraction, molecular packing and/or capillary condensation occurs readily, as with carbon tetrachloride and water on carbon. In the latter case, the pore size distribution determines the adsorptive capacity of the adsorbent.

The surface areas, as reported in Table 4-VI, are based on nitrogen adsorption data using the Brunauer, Emmett and Teller (BET) method (Brunauer 1938). On the per-unit-weight basis, the surface areas of activated carbons are considerably larger than those of the polar adsorbents. Activated carbons used for vapor adsorption range in area from 1100 to 1600 m^2/g, with all types ranging from about 600 to 1600 m^2/g. Silica gels and activated alumina range from 800 m^2/g downward to about 200 m^2/g.

Adsorbent Porosity - The pore size distribution, mean pore diameter, surface area and pore volume are parameters that define the pore structure. In Tables 4-VI and -VII, the pore volume for each adsorbent was obtained by subtracting the nonporous, or impervious volume from the volume of the particles. The impervious and particle volumes were obtained from the particle and true densities as given. The mean pore diameters for silica gel and activated alumina were calculated assuming a cylinder of volume and surface as given. The mean micropore diameter range for the activated carbons was selected from pore size distribution curves shown in Figures 4-1 and -2.

For the silica gels, activated aluminas and activated carbons, the mean pore diameters are in the 15 to 22 Å range. Molecules of concern in air pollution range in diameter from 3.6 to over 8.7 Å; a partial list of pollutant molecular diameters is given in Table 4-V. In view of the relatively small difference between the molecular and pore diameters, the opposite-wall effects play an important role in the pollutant vapor adsorption process. Adsorptive capacity is determined by the pore space occupied by the pollutant liquid volume. The probability of molecular packing decreases with increasing pore diameter; the largest pore diameters in which liquid packing can occur at low relative vapor pressures vary with molecular diameter and adsorptive affinity, but would be in the range of 20 to 30 Å. Adsorption at high relative vapor pressures proceed in the large pores (30 to 100,000 Å) by multilayer adsorption and capillary condensation. Most pollution control problems are, however, concerned with emission rates at low relative vapor pressures; therefore, the small-pore volume is the prime factor in determining the adsorbent effectiveness.

Activated Carbon Pore Size Distribution - Because of the prevalence of moisture in pollutant airstreams, the use of polar adsorbents is very limited in pollution control, while activated carbons are successfully used in many applications. In further discussions on adsorbents, the emphasis is on activated carbons, although much of the information presented will also be applicable to polar adsorbents.

In Figures 4-1 and -2, pore size distribution curves are presented for four activated carbons of greatly different adsorptive capacities. These four curves essentially span the gamut of distributions observed in carbons. For discussion purposes, the pores less than 30 Å diameter are designated as micropores and those that are larger, macropores. Dubinin (1936) has classified pores below 20 Å diameter as micropores, those larger than 200 Å as macropores and those between 20 and 200 Å as transitional pores.

Curve I is for a granular Darco carbon developed by Atlas Powder Company for aqueous phase adsorption usage. The open pore structure (i.e., the large macropore volume) is highly desirable since it accelerates the liquid phase

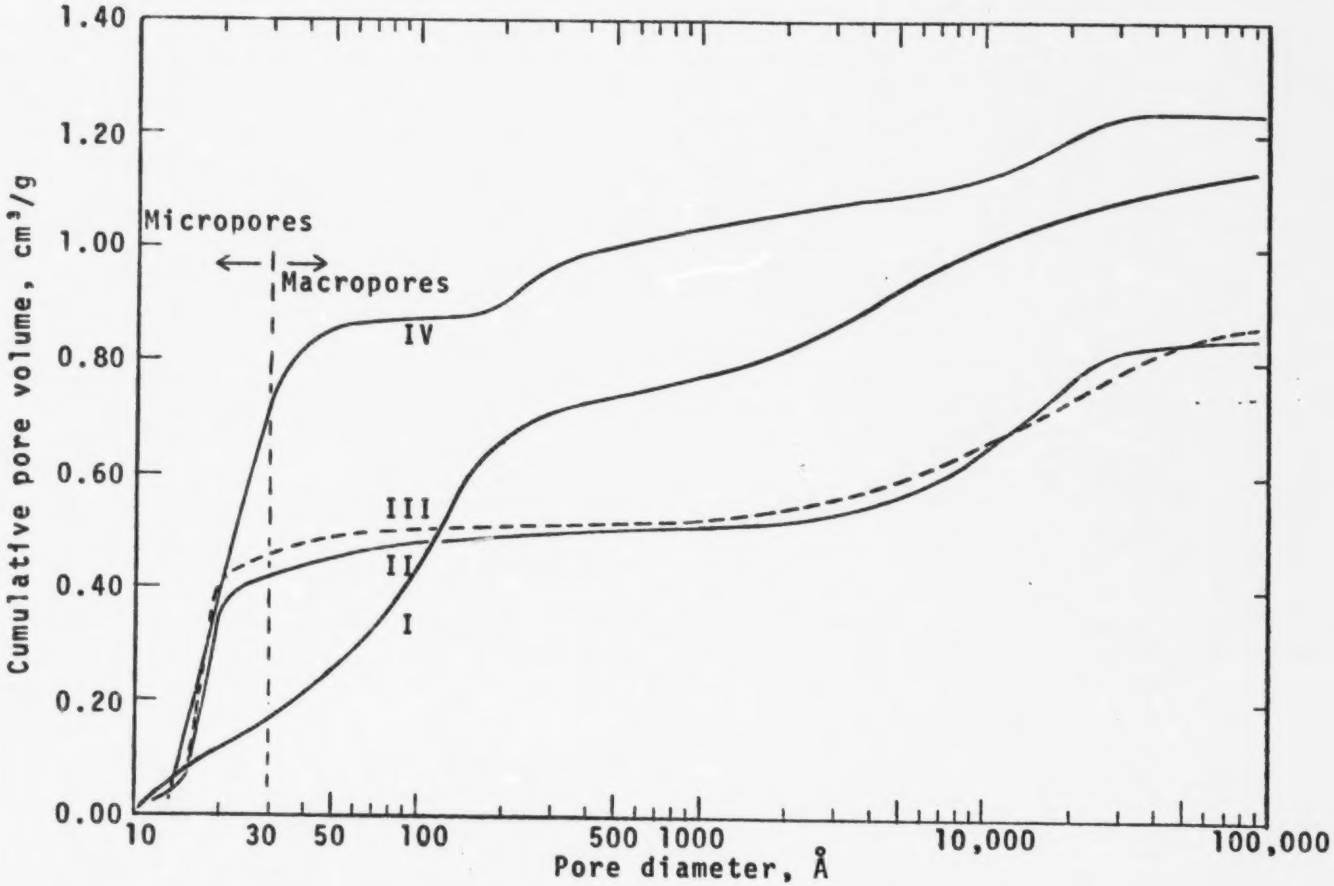


Figure 4-1 Pore Size Distribution Curves For Activated Carbons with Cumulative Pore Volume Calculated Per Unit Carbon Weight I Darco Carbon, IV Superactivated Coconut, II Type BP Pittsburgh Activated Carbon, and III Type SXA Union Carbide Corp.

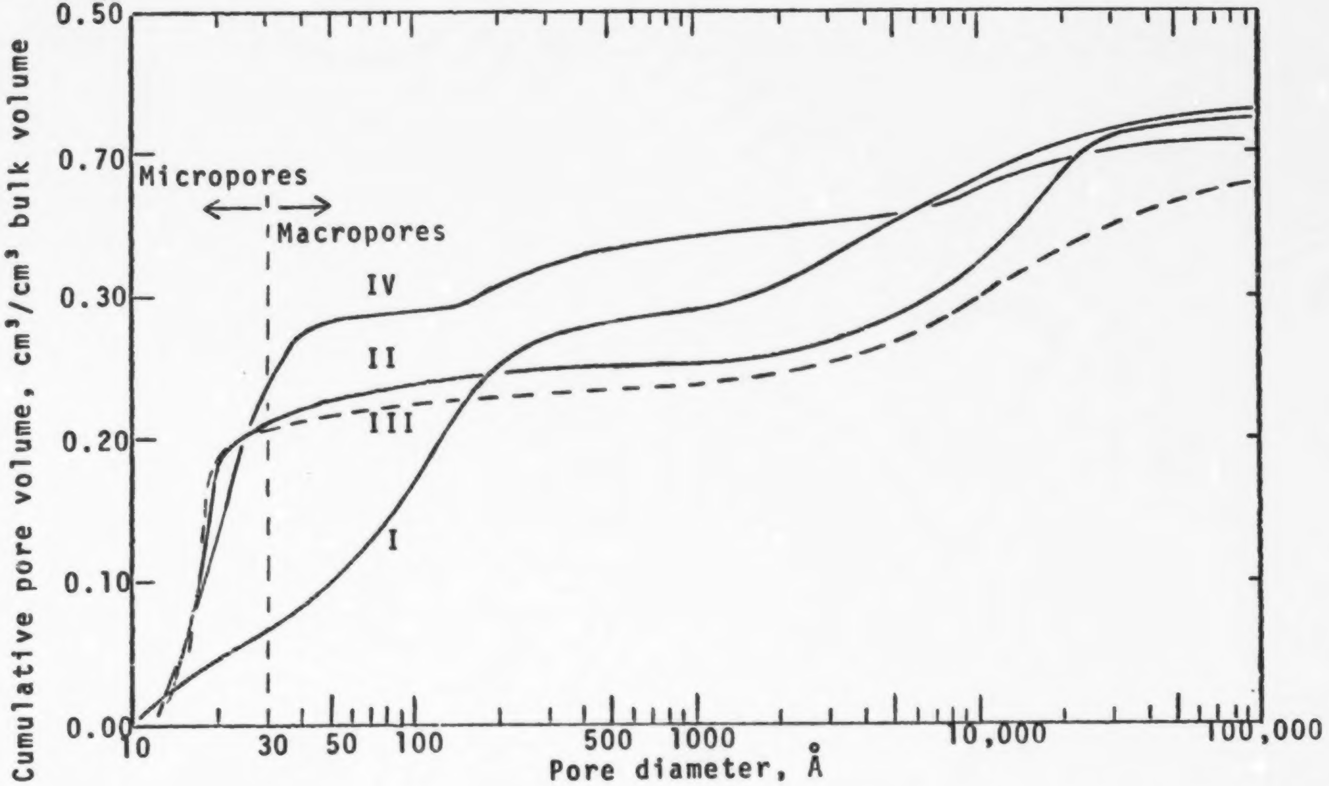


Figure 4-2 Pore Size Distribution Curves For Activated Carbons with Cumulative Pore Volume Calculated Per Unit Carbon Bulk Volume Basis, I Darco Carbon, IV Superactivated Coconut, II Type BP Pittsburgh Activated Carbon, and III Type SXA Union Carbide Corp.

adsorption rate which is generally very slow. The small micropore volume of 0.18 cm^3/g greatly limits the capacity of this carbon for vapor adsorption; therefore, the carbon is not competitive with the other carbons represented in the Figures 4-1 and -2.

Curve IV represents the other extreme in adsorptive capacity. The micropore volume is 0.73 cm^3/g and is approaching the upper limit attainable. This was a highly active Barnebey Cheney coconut carbon that was further activated (superactivated) in an attempt to reach the ultimate in capacity. The yield was very low, less than 1% of starting material, which makes its cost of manufacture excessive.

Curve II is for a type BP carbon manufactured by the Pittsburgh Activated Carbon Company; curve III is for a type SXA manufactured by the Union Carbide Corporation. These carbons occupy the middle of the capacity range with micropore volumes of 0.42 and 0.46 cm^3/g, respectively. The BP carbon is used in considerable quantities in military gas masks and the SXA, in air purification and solvent recovery systems. These two distribution curves are characteristic of carbons economically best applicable to air pollution control.

The carbon tetrachloride activity test, which is most frequently used to determine the suitability of a carbon for vapor adsorption, measures the micropore volume. Under the test conditions the liquid volume of carbon tetrachloride adsorbed is very nearly equal to the micropore volume. Shown below are comparative figures of carbon tetrachloride test results and micropore volumes of the four carbons:

Carbon	Carbon tetrachloride activity		Micropore
	g/g	cm^3 liq/g	volume, cm^3/g
I	0.30	0.20	0.18
II	0.68	0.45	0.42
III	0.73	0.48	0.46
IV	1.20	0.79	0.73

Since the micropore size distributions of different carbons vary, as illustrated in the Figures 4-1 and -2, the adsorptive capacities of carbons of equal carbon tetrachloride activity will only agree at one relative vapor pressure for any vapor. For carbon tetrachloride the point of agreement is at 0.16 relative vapor pressure. Carbons with smaller mean micropore diameters will adsorb vapors more strongly at the lower relative vapor pressures.

Adsorptive Capacity of Operating Unit - The various properties of the adsorbents are reported on the per-unit-weight basis in the manufacturers' sales literature, although the adsorbents are used in various operating units on the fixed volume basis. Unlike the weight basis, the bulk volume basis would vary with mesh size, mesh size distribution, particle shape and the method of packing the adsorbent bed. A comparison of properties on the weight basis is a simpler and more reliable evaluation of the relative merits of the different adsorbents.

To determine the true effectiveness of an adsorbent in actual usage, the various physical and adsorptive properties need to be recalculated on the per-unit-volume basis as has been done in Tables 4-VI and -VII. When comparing the surface area in m^2/g with m^2/cm^3 bulk volume, and pore volume in cm^3/g with cm^3/cm^3 bulk volume, much of the large apparent advantage of carbons over polar adsorbents is greatly reduced. Similarly, the comparison of micropore volumes on the weight basis with those on the bulk volume basis tends to nullify the large apparent advantage of Carbon IV over Carbons II and III.

Table 4-VIII shows the effect on carbon tetrachloride activity and surface area when the values are converted to bulk volume basis. Less weight of the lighter Type IV carbon is required to fill the adsorption operating unit and thereby maintain cost closer to the other heavier carbons.

Table 4-VIII Physical Properties of Activated Carbons, Densities, Carbon Tetrachloride Activities and Surface Areas

Carbon	Bulk density, g/cm^3	Carbon tetrachloride activity g/g	Carbon tetrachloride activity g/cm^3	Surface area m^2/g	Surface area m^2/cm^3
I	0.38	0.30	0.11	580	220
II	0.50	0.68	0.34	1100	550
III	0.45	0.73	0.33	1300	580
IV	0.33	1.20	0.40	1600	530

Theories of Adsorption

Forces of Adsorption

Van der Waals' Forces - The forces active in physical adsorption on polar and nonpolar adsorbents are associated with van der Waals' forces as measured by constant a in the van der Waals' equation of state; see Appendix D. This association was first observed by Arrhenius (1912). Various investigators since then have derived mathematical expressions that offer explanations of the origins of these forces. These theories have not lead to useable methods for predetermining the adsorptive affinity from fundamental properties of the adsorbed vapor and adsorbent surface. Among the complicating factors are (1) the surface nonuniformities, (2) contribution of subsurface atoms to the adsorption potential, (3) uncertainty of distance between the adsorbed molecule and the surface, and (4) opposite-wall effects in small pores.

Orientation and Induction Effects - To account for the van der Waals' attraction between polar molecules, the dipole moment and the polarizability are regarded as the primary forces. The first is often referred to as the orientation effect and was investigated by Keesom (1921); and the second, investigated by Debye (1920), is referred to as the induction effect. Lorenz and Landé, in applying the orientation effect to adsorption, derived an adsorption potential equation on the assumption that an interaction occurs between the dipoles and a mirror image of the dipole in a polarizable surface. Jaquet (1925) followed the same line of reasoning but also included the induction effect. According to Jaquet, the adsorption potential, Q, at low temperatures is

$$Q = -\frac{N\mu^2}{(2\sigma)^3}\,\frac{2}{1-2n} = -\frac{N\mu^2}{4\sigma^3-\alpha} \qquad (4\text{-}1)$$

where $n = \alpha/(2\sigma)^3$, α is the polarizability, N is Avogadro's number, μ is the dipole moment and σ the distance of adsorbed molecule to adsorbent surface. At low temperatures where thermal agitation is small, the dipoles are all oriented perpendicular to the surface. At high temperatures where all orientations are equally probable, the adsorption potential is

$$Q = -\frac{N\mu}{(2\sigma)^3}\,\frac{2}{3}\left[\frac{1}{1-2n} + \frac{1}{1-n}\right] \qquad (4\text{-}2)$$

The orientation and induction effects do not account for the adsorption of nonpolar molecules, particularly to nonpolar surfaces.

Dispersion Effect - London (1937) attributed the attraction between nonpolar molecules to fluctuating dipoles caused by momentary changes in electron distribution about the atomic nuclei. The fluctuating dipoles induce dipoles in neighboring molecules which then fluctuate in phase with each other. The resulting attraction is referred to as the dispersion effect, and the potential between two molecules of the same type is approximately expressed by the equation

$$Q = -\frac{3}{4}\frac{1}{\sigma^6} h\nu\alpha^2 \qquad (4\text{-}3)$$

where h is the Plank's constant and ν is the characteristic frequency of oscillation of the molecule, the same as in the Sellmier light dispersion equation. For simpler molecules $h\nu$ is almost equal to the ionization energy; but for larger molecules, particularly if they contain chromophoric groups, $h\nu$ may be considerably different from the ionization potential.

With reference to Equations 4-1 and -2, the induction effect, determined by the polarizability α, is always small, while the orientation effect varies directly as the dipole moment μ, or as μ to the second power. For small polar molecules the orientation potential is large; but for increasingly larger molecules the dipole moment decreases rapidly and thereby the orientation potential also decreases. For most of the organic pollutants of concern, the orientation potential is essentially zero. The dispersion potential is dominated by the polarizability, and, because polarizability is proportional to the molar volume (V_m), the dispersion potential increases with molecular size, but with minor variations produced by $h\nu$. This means that small nonpolar molecules are not strongly adsorbed by any of the adsorbents by the van der Waals' forces. These theories are in essential agreement with observed adsorptive affinity variations as presented in Tables 4-II and -III.

Adsorptive Capacity

In the prior text of this chapter, the effects of chemical constitution of the adsorbent, its pore structure and the chemical nature and size of the vapor molecule were discussed relative to the adsorptive affinity. These factors are considered in selecting the type of adsorbent that is best suited for the particular pollution control problem under consideration.

One of the parameters that determines the effectiveness of the selected adsorbent is its adsorptive capacity under the expected operating conditions. This information is necessary before any sizing estimates can be made for the sorption unit. In a general sense, the capacity increases with increased vapor pressure and decreases with increased temperature.

Methods for plotting adsorption data and adsorption equations have been developed which: (1) make presentation of data concise and convenient, (2) permit extrapolation of data to unmeasured pressures and temperatures, and (3) permit prediction of adsorptive capacities of unmeasured vapors from few data on those that have been measured. The last item is of great importance in pollution control work because of the large number of different vapors of concern that are emitted under a wide variety of conditions and for which adsorption data are lacking or very meager.

Adsorption Isotherms - Adsorption at constant temperature is frequently plotted on a linear graph as a function of vapor pressure or relative partial pressure (p/p_o). Figure 4-3 shows a family of hydrocarbon isotherms on activated carbon plotted in this manner. The amount adsorbed increases rapidly with increased pressure at the low pressure end of the isotherm but levels off at the higher pressures. The liquid volume, 0.43 cm^3 liq/g, at 760 mm of Hg pressure for butane is approaching the micropore volume; hence, the diminished adsorption is caused by filling up the small pores. At higher pressures approaching p/p_o near one, adsorption would continue with the filling up also of the macropores. This phase of the adsorption would be accompanied by a considerable change in shape of the isotherm. Macropore filling can only occur at temperature below the critical temperature.

Curve III of Figure 4-1 shows the micropore and macropore size distribution of the type of carbon used in adsorption measurement plotted in Figure 4-3. At 760 mm of Hg pressure for butane, $p/p_o = 0.28$.

Only the very low pressure end of each isotherm in Figure 4-3 would be of direct interest in pollution control problems. Pollutant vapor concentrations at the sources of emission are generally below 1,000 ppm, and combustible solvent concentration, for safety reasons, is maintained at or below the 25% lower explosive limit during recovery operations. Table C-I gives LEL concentrations for pollutants of concern. The 25% LEL for most organic vapors is below 13,000 ppm which in pressure units corresponds to 10 mm of Hg.

When it is necessary to present adsorption data over a wider pressure range than the single order of magnitude shown in Figure 4-3, the adsorption data are plotted on a

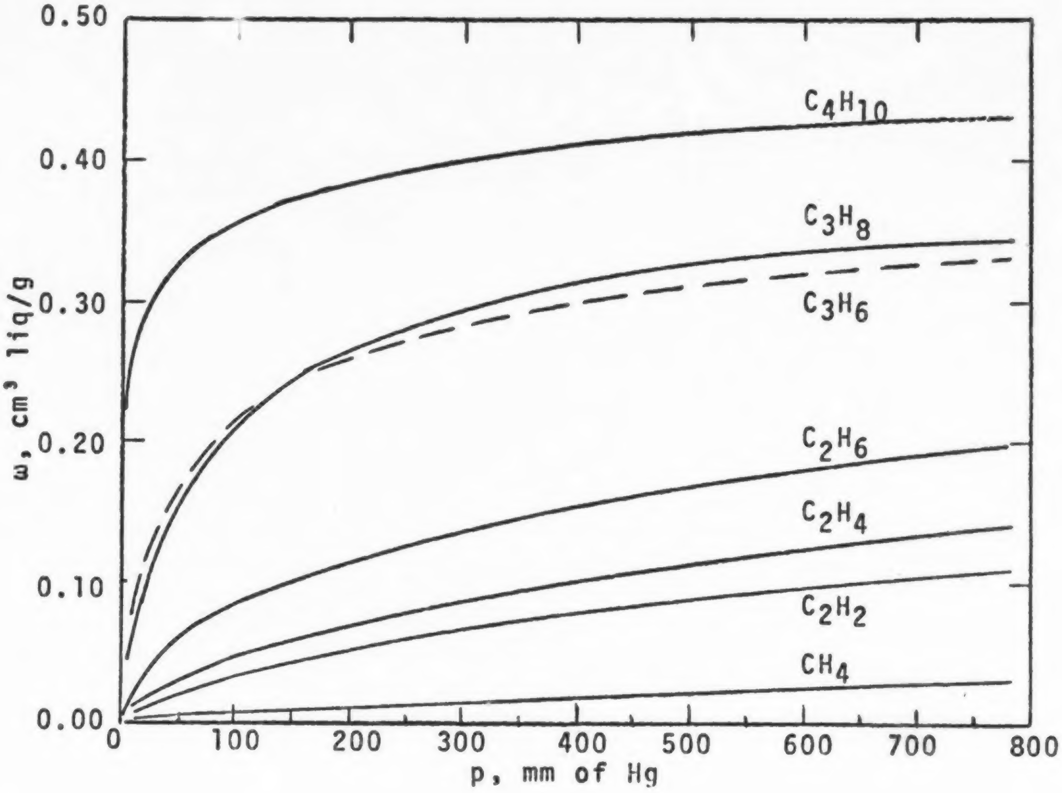


Figure 4-3 Adsorption Isotherms of Hydrocarbon Vapors, Amount Adsorbed ω at Pressure p on Type Columbia L Carbon at 100°F, Liquid Volume of ω at Boiling Temperature.

log-log graph as in Figure 4-4. These isotherms also level off at the higher pressures because of micropore filling at the 0.50 cm^3/g level. In the low pressure region below 10 mm of Hg, which is of interest in pollution control, this manner of plotting clearly indicates the adsorptive capacities.

Isotherms of a different type that are important to pollutant vapor control are those of water vapor on activated carbon. The nature of the isotherm gives some insight into the type of interference the presence of water vapor will have on the adsorption of organic vapors. Isotherm I of Figure 4-5 corresponds to pore size distribution Curve I in Figures 4-1 and -2. Isotherm II is typical for activated carbons best suited for adsorption of vapors; i.e., of carbon types represented by Curves II and III in Figures 4-1 and -2.

The characteristic features of the water adsorption isotherm are the pronounced hysteresis of the adsorption and desorption branches and the rapid increase in amount adsorbed at p/p_o above 0.5. At p/p_o below 0.4 the moisture in a pollutant airstream will cause very little interference with the adsorption of most of the pollutants of concern. Moisture can cause a further decrease of the already poorly adsorbed organic vapors such as chloromethane, ethane and methane. Organic vapors of V_m greater than 90 cm^3/mol displace water from the carbon, but at the higher p/p_o of water the adsorption rate of organic vapors decreases. In thin carbon beds, a high water p/p_o can cause a premature pollutant vapor penetration. Moisture interferes less with water soluble pollutants than with nonsoluble pollutants.

The hysteresis can cause operational problems. If satisfactory operation is possible at p/p_o range from 0.5 to 0.7, but the moisture content of the pollutant airstream should happen to go to higher humidities such as to saturate the bed, the carbon would have to be dried to p/p_o of 0.4 or less before satisfactory operation can be regained.

Equations for Isothermal Adsorption - Various investigators have developed adsorption equations that agree with data for specific adsorbate-adsorbent systems and over fairly limited concentrations. These equations are suitable for interpolation and extrapolation purposes.

An equation found applicable for liquid phase decolorizing applications and also frequently checked out on vapor-phase adsorption data is the Freundlich (1933) equation as given below in logarithmic form.

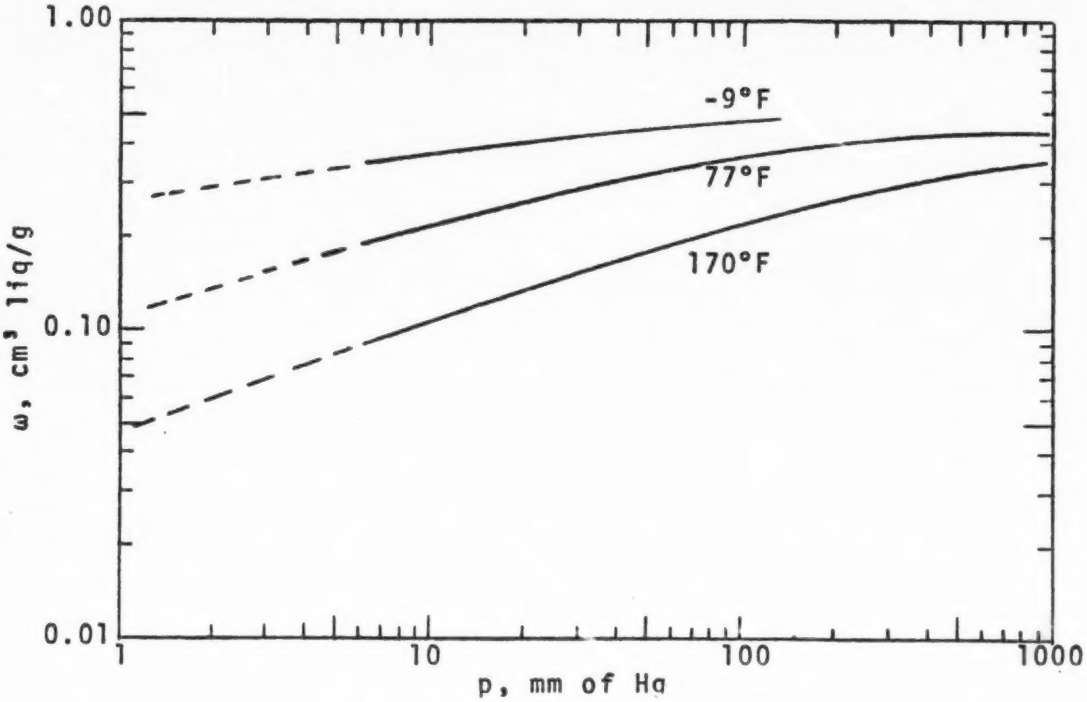


Figure 4-4 Adsorption Isotherms of Butane at Three Temperatures on Pittsburgh BPL Type Carbon, Amount ω Adsorbed at Pressure p. Data From Grant (1962)

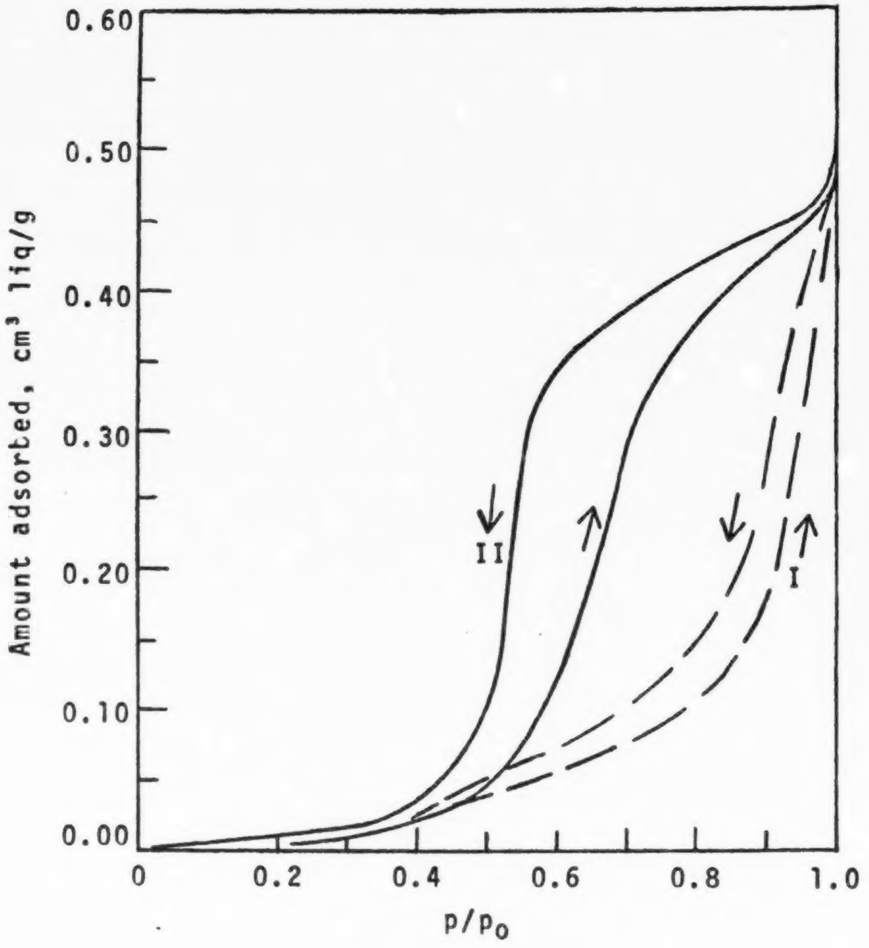


Figure 4-5 Isotherms of Water on Activated Carbons Showing Hysteresis Between Adsorption and Desorption Branches, I Darco Carbon, II Typical of Pittsburgh BP or Union Carbide SXA.

$$\log \omega = \log k + [1/n] \log p \qquad (4\text{-}4)$$

Here k and n are constants dependent on molecular structure of adsorbate, chemical constitution of adsorbent, pore structure and temperature; k is equal to ω when p is one.

When the adsorption data obey the equation, a log-log plot yields a straight line graph. The type of curves in Figure 4-4 are frequently called Freundlich isotherms; however, in these cases, the curvatures show deviation from the equation. At lower pressures, below 1 mm of Hg, the tendency is for the curves to straighten out.

In 1916, Langmuir derived an adsorption equation for vapors on kinetic considerations. According to Langmuir, vapor molecules colliding with the adsorbent surface suffer inelastic collisions; the time lag is responsible for adsorption. He also assumed that only unimolecular layer adsorption could occur. The Langmuir equation is presented in two forms below; the latter is more convenient for testing against adsorption data.

$$v = \frac{v_m\ bp}{1 + bp} \qquad (4\text{-}5)$$

$$\frac{p}{v} = \frac{1}{v_m b} + \frac{p}{v_m} \qquad (4\text{-}6)$$

In these equations v is the volume of vapor adsorbed on a unit weight of adsorbent, b is a constant, and v_m is the amount of vapor necessary to form a unimolecular adsorbed layer. The equation fits chemisorption data and physical adsorption data at low relative pressures or data of gases at temperatures above their critical temperatures. Essentially all pollutant vapors are adsorbed below their critical temperatures and on adsorbents of small pore diameter in which opposite pore wall attractive forces would induce adsorption by molecular packing rather than unimolecular adsorption. The equation has little or no direct application in pollution control studies; but it is an important equation used in developing later equations useful to pollution control.

Brunauer, Emmett, and Teller (1938) derived equations for multilayer adsorption of vapors by generalizing on Langmuir's treatment of unimolecular adsorption. On powdered materials or adsorbents having large pores, where an unrestricted number of molecular layers can be adsorbed; the equation has the form

$$\frac{p}{v[p_o-p]} = \frac{1}{v_m c} + \frac{c-1}{v_m c}\frac{p}{p_o} \qquad (4\text{-}7)$$

In this equation c is a constant dependent on temperature, the average heat of adsorption E_1 in the first adsorbed layer, and the heat of liquifaction E_ℓ.

$$c = \exp \frac{[E_1-E_\ell]}{RT} \qquad (4\text{-}8)$$

When the adsorption data obey the equation, a plot of

$$\frac{p}{v[p_o-p]} \text{ versus } \frac{p}{p_o} \qquad (4\text{-}9)$$

gives a straight line graph from which it is then possible to calculate v_m and c. The number of molecules in v_m multiplied by the surface area covered by a single molecule gives the total surface area of the adsorbent. This is the well known BET equation, and, amongst many other applications, is used by the adsorbent manufacturers to determine and report the surface areas of their products. It has been the center of considerable investigation by numerous researchers whose works have been reviewed by Gregg and Sing (1967).

For surface area determinations, the most practical gas is nitrogen and the adsorption data are obtained at liquid nitrogen temperature, i.e., -196°C. The nitrogen molecule mean diameter is 4.3 Å, and the area covered by each molecule is 16.2 square Å. In adsorbents having small pores, particularly in activated carbons, the nitrogen molecule diameter is a large fraction of the pore diameter; as for instance in pores less than 17 Å diameter (the mean diameter for SXA and BP Figure 4-1) the ratio is over 0.25. In these cases, the plot of relationship (4-6) above gives a very short straight line graph or one that has a continual but slight curvature; hence, the surface areas reported for these adsorbents are subject to some error. The BET equation developed for a flat surface deviates when applied to small-pore-sized adsorbents. When the bulk of the pores are 30 Å and larger, the plot of relationship (4-6) gives a straight line graph that can extend to 0.35 p/po, and thereby lend a greater confidence level in these applications.

Where the number of molecular layers is restricted to some finite number n, as might be the case in small-pore-sized adsorbents, the BET equation has the form

$$v = \frac{v_m cx}{1-x} \frac{1-(n+1)x^n + nx^{n+1}}{1+(c-1)x - cx^{n+1}} \qquad (4\text{-}10)$$

where $x = p/p_0$. This equation, however, has not found acceptance among adsorption investigators as an equation for determining the surface area.

Pore Structure Determination

Based on Nitrogen Adsorption Data - The pore size distribution is one of the most important factors that determine the overall shape of the isotherm, and conversely the isotherm should give a measure of the pore size distribution when correctly interpreted.

According to multimolecular layer and capillary condensation theories, the adsorption of a gas such as nitrogen at the nitrogen boiling point (-196°C) commences as a unimolecular layer followed by multimolecular layers until the pore space is filled. This mechanism determines the shape of the adsorption branch of the isotherm. On desorption, the nitrogen is released by a different mechanism that gives a hysteresis loop to the desorption branch of the isotherm. The general form of a nitrogen isotherm is illustrated in Figure 4-6 for an activated carbon suited for vapor phase adsorption.

When an incremental volume of adsorbed nitrogen (liquid volume) is desorbed, a part of it is vaporized from the multimolecular layer on the pore wall and a part from the meniscus of the condensed phase in the inner capillary space. The p/p_0 bears relationships simultaneously to the meniscus radius and multimolecular layer thickness. The Kelvin equation (Thompson 1871) given below expresses the function between p/p_0 and meniscus radius, r_k.

$$r_k = \frac{2\gamma\ V\cos\phi}{RT\ \ln(p_0/p)} \qquad (4\text{-}11)$$

Here γ is the surface tension of the adsorbed nitrogen, V the liquid molar volume of the adsorbed nitrogen, and ϕ the contact angle of the miniscus with the multimolecular adsorbed layer. (For nitrogen at -196°C, ϕ is zero). The multimolecular layer thickness, τ, can be determined experimentally for nonporous adsorbents and then applied to porous adsorbents assuming the function still applies. The pore radius at any p/p_0 on the desorption branch of the

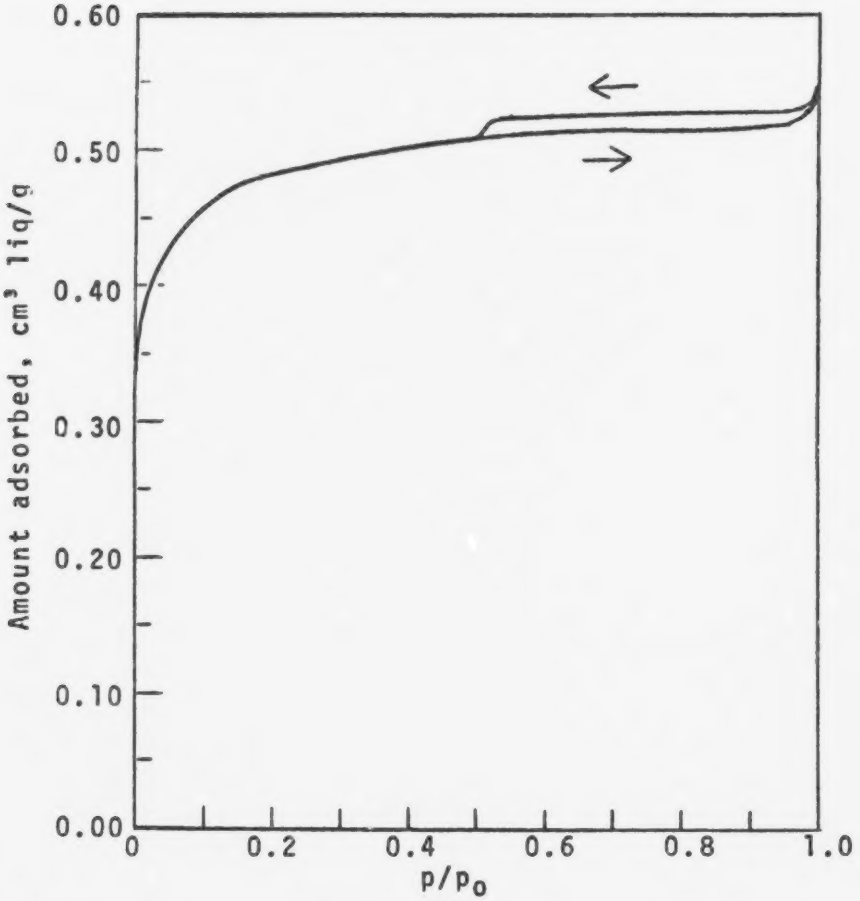


Figure 4-6 Nitrogen Isotherm on Activated Carbon at -195°C Showing Hysteresis Loop Extending from p/p_0 = 0.5 to 1.0

isotherm is then

$$r = r_k + \tau \; . \qquad (4\text{-}12)$$

Barrett, Joyner and Halenda (1951), on these basic assumptions, developed a method for determining pore size distribution curves for adsorbents from the desorption branch of the nitrogen isotherm determined at -196°C. The calculations are quite involved requiring tables of precalculated τ vs p/p_0 values (American Document Institute). The method, on theoretical grounds, is applicable only to the portions of the isotherm above the lower p/p_0 at which the hysteresis loop closes. The lower limit can range from 0.4 to 0.5 p/p_0; the 0.4 p/p_0 corresponds to 40 Å pore diameter.

Because of difficulties in measuring p/p_0 accurately above 0.97, the practical upper limit on diameter determinations is 670 Å. The method has, however, been extended by many investigators to pores smaller than 40 Å.

Based on Water Adsorption Data - An alternative method applicable only to activated carbons involves the direct application of the Kelvin equation (Equation 4-11) to the desorption branch of the water isotherm (Juhola and Wiig, 1949). The pore size distribution is derived by measuring desorbed liquid water volume increments at each reduced p/p_0. In Equation 4-11, molar volume V varies between 19.3 and 21.2 cm³/mol with changing p/p_0 (Wiig and Juhola, 1949) and cos ϕ is equal to 0.49. This method is applicable for determining the pore diameters from about 670 Å down to 10 Å.

To obtain the most reliable results with this method chemically active and polar groups must be leached out of the carbon and carbon evacuated at 400°C prior to water adsorption measurements.

Mercury Porosimetry - Because of the high surface tension of mercury, and the fact that it is not strongly adsorbed by porous materials commonly used as adsorbents, mercury can be used as a medium for determining the macropore size destribution. By applying increasingly higher pressures, mercury penetrates into pores of decreasing diameter. The relationship between pressure, P, and pore diameter, d, is given by the equation

$$d = \frac{4\gamma \cos\phi}{P} \qquad (4\text{-}13)$$

where γ is the surface tension of mercury and ϕ the contact angle of mercury with the pore wall. The pore size distribution is derived by measuring volume increments of mercury penetration at each pressure increase. This technique was first suggested by Washburn and first used by Ritter and Drake (1945). They found that ϕ was equal to 140° on a variety of solids although some uncertainty exists in its magnitude.

The largest pores measurable are 100,000 Å at a pressure of 17.4 lb/sq in. absolute. A pressure of this magnitude is required to outline adsorbent granules; or conversely, "pores" larger than 100,000 Å diameter are in reality indentations in the granule exterior surfaces. The smallest pores measurable depend on maximum pressure attainable and the effect the pressure has on the pore structure. A theoretical pressure of 60,000 lb/in^2 is required for mercury penetration into pores of 30 Å diameter. At these pressures compression of the carbon can be expected resulting in erroneous volume measurements. Measurement up to 60,000 lb/in^2 are, however, made as standard practice with commercially available equipment.

Comparison of the Three Methods - The pore size distribution, as determined by the above described three methods, overlap in the 30 to 760 Å diameter which makes possible their comarison over a limited range of application.

Joyner, Barrett and Skold (1951) compared the pore size distribution curves obtained by the nitrogen isotherm method and mercury porosimetry over the diameter range 60 to 600 Å. Their studies were with bone chars and synthad, a material chemically similar to bone char. These adsorbents were chosen because they had an abundance of pores in the range where the two methods overlap. They found a good agreement between the two methods on some of seven adsorbents tested. Where there was more than one peak in the distribution curve both methods indicated their presence, shape and size with good agreement in some cases, although in others, there was displacement.

Pore distributions in the 10 to 600 Å range for activated carbons, as determined by nitrogen and water adsorption methods, yield curves of the same overall shape but disagree to some extent on magnitude of diameter at any given accumulative volume. The most significant variance starts at the 40 Å diameter and is carried down to the smallest pore measured (Juhola, Palumbo and Smith, 1952).

Comparisons of pore size distributions as determined by the water adsorption and mercury porosimetry methods always show a qualitative agreement in shape of distribution curve, but vary in agreement on magnitude of pore diameter at any given accumulative volume. With some carbons, the overlapping section by the two methods coincide; while with others, the variance can be either way.

The conclusion is that the three methods are in agreement in indicating the type of pore structures for diverse carbons. The type of distribution has an important bearing on the adsorption of pollutant vapors at low concentrations. Carbons with an abundance of small pores have the largest capacity at low concentrations, a desirable property for pollutant control; however, an abundance of small pores is an undesirable property in solvent recovery carbons operated at high solvent concentrations.

Adsorption Thermodynamics

Heat of Adsorption - Adsorption is accompanied by two energy changes: (1) a decrease in free energy ΔF measured by the decrease in vapor pressure, and (2) a decrease in entropy ΔS due to decrease in mobility of the adsorbed vapor. These changes decrease the heat content ΔH of the system in the manner expressed by the equation

$$\Delta H = \Delta F + T\Delta S \tag{4-14}$$

All adsorption processes are exothermic.

ΔH can be determined calorimetrically, or more conveniently, from adsorption isotherms measured at separate temperatures by application of the Clausius-Clapeyron equation,

$$\ln p = \frac{\Delta H}{RT} + k \tag{4-15}$$

This equation applies at a constant amount of adsorbed vapor and applies over a limited temperature range because of a gradual variation in ΔH with change in temperature.

Its application can be demonstrated with data taken from Figure 4-4. Table 4-IX presents the pertinent data and the calculated ΔH and k. Sample calculations are given in Appendix E, page E-1.

Table 4-IX Adsorption Data and Calculated ΔH and k for Butane on Activated Carbon Type BP

	p, mm of Hg				
ω, cm³ liq/g	-9°F	77°F	170°F	-ΔH,cal/mol	k
0.20	---	7.3	68	8,800	16.8
0.30	2.3	38	340	8,700	18.3
0.40	17	220	---	7,900	18.7
[liquid]	[300]	[1820]	[7000]	[ca 5,500]	[16.7]

ΔH in these cases are the differential or isosteric heats of adsorption. They decrease as the amount of adsorbed vapor is increased. When the pore space is almost completely filled, ΔH will approach the heat of liquifaction, which varies from 5,600 at -9° to 5,400 cal/mol at 170°F.

The heat of adsorption in the initial stages is the highest because the vapor first becomes attached to the most active sites on the surface or first becomes located in the smallest pores where the opposite wall attractions are the strongest. In the final stages of adsorption, where the adsorption mechanism can be multimolecular layer or capillary condensation in large pores, the heat of adsorption approaches that of liquifaction.

The heats of adsorption increase on the molar weight basis, but when converted to unit weight or unit liquid volume basis, they are in a fairly narrow range, i.e., 100 to 200 cal/g or 200 to 300 Btu/lb of vapor adsorbed. At low pollutant vapor concentrations, below 100 ppm, the heat release rate is slow and is greatly moderated by the airflow. When the vapor concentrations are at the 25% LEL, considerable heating of the carbon bed can occur. Autoignition of carbon beds used for ketone recovery have been reported. This problem is avoided by leaving the bed wet from the prior steam regeneration.

Figure 4-7 shows the data of Table 4-IX plotted as isosteres. When pressure data are available for a given ω at more than two temperatures, a plot of this type measures the degree of agreement with theory. The three pressure points for $\omega = 0.30$ cm^{3}liq/g yield a straight line curve indicating that ΔH is quite constant over the temperature range -9° to 170°F. Carbon adsorbent systems for pollutant control and solvent recovery are operated most effectively in the 60° to 130°F temperature range.

Free Energy Change - The free energy change ΔF, as part of Equation 4-14, is a function of the relative vapor pressure given by the following relationship.

$$\Delta F = -RT \ln[p_o/p] \qquad (4\text{-}16)$$

On the basis of the data in Table 4-IX ΔF values were calculated to show their characteristics; these ΔF values are given in Table 4-X. For these calculations, p_o at -9°F is 300 mm, p_o at 77°F is 1820 mm and p_o at 170°F is 7000 mm of Hg.

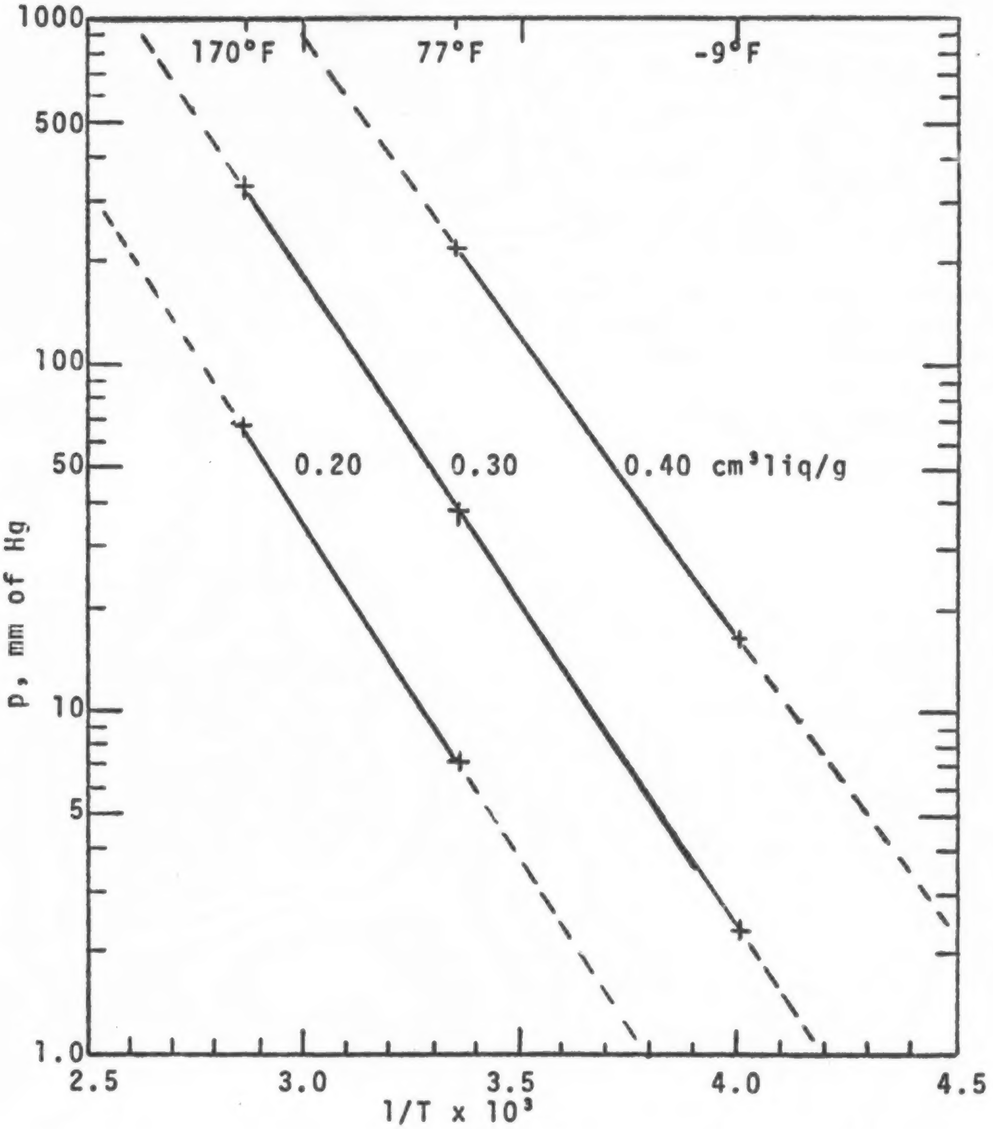


Figure 4-7 Isosteres for Butane on Activated Carbon, Type BP

Table 4-X Free Energy Change ΔF During Adsorption of Butane on Activated Carbon

ω, cm³ liq/g	-ΔF, cal/mol at -9°F	77°F	170°F
0.20	-----	3,300	3,200
0.30	2,400	2,300	2,100
0.40	1,400	1,200	-----

ΔF decreases as the amount of vapor adsorbed on the carbon is increased. At complete filling of the pores, ΔF approaches zero and ΔH = TΔS.

Entropy Change - Table 4-XI gives the entropy changes for the butane adsorption obtained by substitution of ΔH and ΔF from Tables 4-IX and -X into Equation 4-14.

Table 4-XI Entropy Change ΔS During Adsorption of Butane on Activated Carbon

ω, cm³ liq/g	-ΔS, cal/mol -9°F	77°F	170°F
0.20	-----	18.6	16.0
0.30	25.2	21.6	18.8
0.40	26.0	22.6	----
[liquid]	[22.4]	[18.4]	[16.0]

ΔS measures the change in mobility of the molecules in transfer from the vapor phase to the adsorbed phase. A large -ΔS indicates a large decrease in mobility while a +ΔS indicates a large increase. As the micropores are filled -ΔS increases and is maximum at the point where the micropores are completely filled, i.e., at about 0.45 cm³/g. During macropore filling -ΔS decreases and ultimately reaches the value at normal condensation.

Potential Theory Equations - Two properties of ΔF useful in pollution control work are: (1) ΔF is fairly constant over a moderate temperature range; and (2) ΔF decreases with increased amount of adsorbed vapor. Equations have been developed on the basis of these two properties that permit estimating adsorptive capacities for an unmeasured vapor when meager data are available on some other, but similar, vapor.

Tables 4-X and -XII and Figure 4-8 present numerical figures that indicate the degree of constancy of ΔF with temperature change, and show the decrease of ΔF with increased ω.

For propane (Table 4-XII) at ω less than 0.20 cm³ liq/g, ΔF increases gradually with increased temperature, while above 0.20, it decreases with increased temperature. At high adsorption pressures p or high vapor pressures p_0, the use of fugacities, f and f_0, in place of p and p_0 in Equation 4-16 improves the constancy of ΔF. Sample calculations showing the use of fugacity and its effect on ΔF are worked out in Appendix E, page E-3.

Table 4-XII Variation of ΔF or ε_i with Temperature and Amount ω of Propane Adsorbed on Type L Carbon

	-ΔF or ε_i, cal/mol				
ω, cm³ liq/g	100°F	150°F	200°F	250°F	Average of 100°F & 150°F
0.10	3,800	4,000	4,200	4,500	3,900
0.15	3,300	3,400	3,600	3,600	3,350
0.20	3,000	3,000	3,100	-----	3,000
0.25	2,600	2,500	-----	-----	2,550
0.30	2,100	2,000	-----	-----	2,050

Equation 4-16 is the basis of the Polanyi potential theory of adsorption, the symbol ε_i being used in place of ΔF (Polanyi, 1914). He observed that at any fixed amount ω adsorbed, ε_i is constant; hence,

$$\frac{\varepsilon_i}{RT} = -\ln[p_0/p] \qquad (4\text{-}17)$$

If p_0/p_1 and T_1 are known at a fixed ω_1, p_0/p_2 can be estimated for ω_1 at T_2 provided T_1 and T_2 are not widely separated. Carbon adsorbent systems are most effectively used in the fairly narrow temperature range of 60° to 130°F; hence, ΔF or ε_i will be fairly constant in the temperature range of interest.

The curves for propane, butane and pentane in Figure 4-8 show graphically the variation of ΔF with molecular size and ω. When ΔF is divided by the molecular weight, i.e., by converting ΔF to cal/g, the three curves are drawn closer together giving a common curve; this effect is shown in

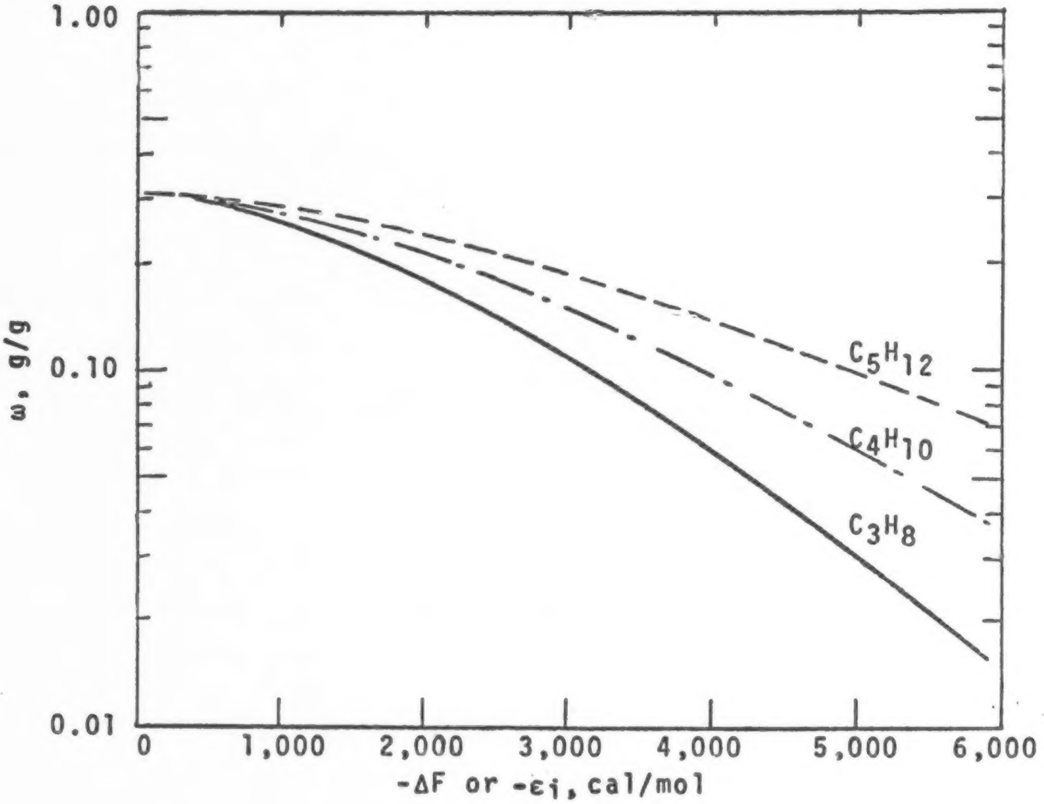


Figure 4-8 Variation of Free Energy ΔF or Polanyi Potential ε_i with Amount of Vapor ω Adsorbed on Activated Carbon. ω Measured per Gram of Vapor and ΔF and ε_i per Mol of Vapor

Figure 4-9. The amount adsorbed is now a function of M, T and p_o/p as shown below,

$$\omega = \text{function of } \frac{RT}{M} \ln (p_o/p) \qquad (4\text{-}18)$$

where M is the molecular weight and ω is measured in g vapor per g of carbon.

If a few adsorption points are known for an activated carbon so that a curve can be drawn, the curve can now be used to estimate isotherms of other members of a homologous series or of other similar vapors.

Because of packing of molecules in the micropores, adsorptive capacity is determined volumetrically rather than gravimetrically. By dividing ΔF by the molar volume, Equation 4-18 is greatly broadened to include other homologous series and a wider range of higher density molecules. The proper choice of molar volume has been an area under considerable investigation amongst different adsorption investigators. Dubinin, et al. (1947) suggested using the liquid molar volume of the adsorbed vapor at the adsorption temperature. Lewis, et al. (1950) and later Grant, et al. (1962) experimented with the molar volume at the temperature where vapor pressure equals adsorption pressure. Robell, et al. (1965) used the liquid molar volume at the normal boiling point. Lewis and Grant used fugacities in place of adsorption and liquid vapor pressures where a significant difference existed.

In view of the packing of relatively large molecules of over 4 Å diameter in pores of less than 20 Å diameter, the normal concepts of liquid molar volumes lose some of their meaning. Two effects can occur: (1) steric hindrance which tends to promote packing of lesser density than in normal liquids, and (2) stronger attraction toward the pore walls which tends to promote packing of greater density than in normal liquids. The actual volume of adsorbed liquid can be expected to vary with molecule-to-pore diameter ratio and compressibility of the molecules.

For purposes of estimating ω, the right side of Equation 4-18 is now modified so that it has the form

$$[T/V] \log [p_o/p], \text{ or} \qquad (4\text{-}19)$$

$$[T/V] \log [f_o/f] \qquad (4\text{-}20)$$

where V is the liquid molar volume of best choice for the particular system. From adsorption data (at least two adsorption points) a generalized adsorption curve is drawn wherein ω in liquid volume per gram of carbon is plotted on a logarithmic

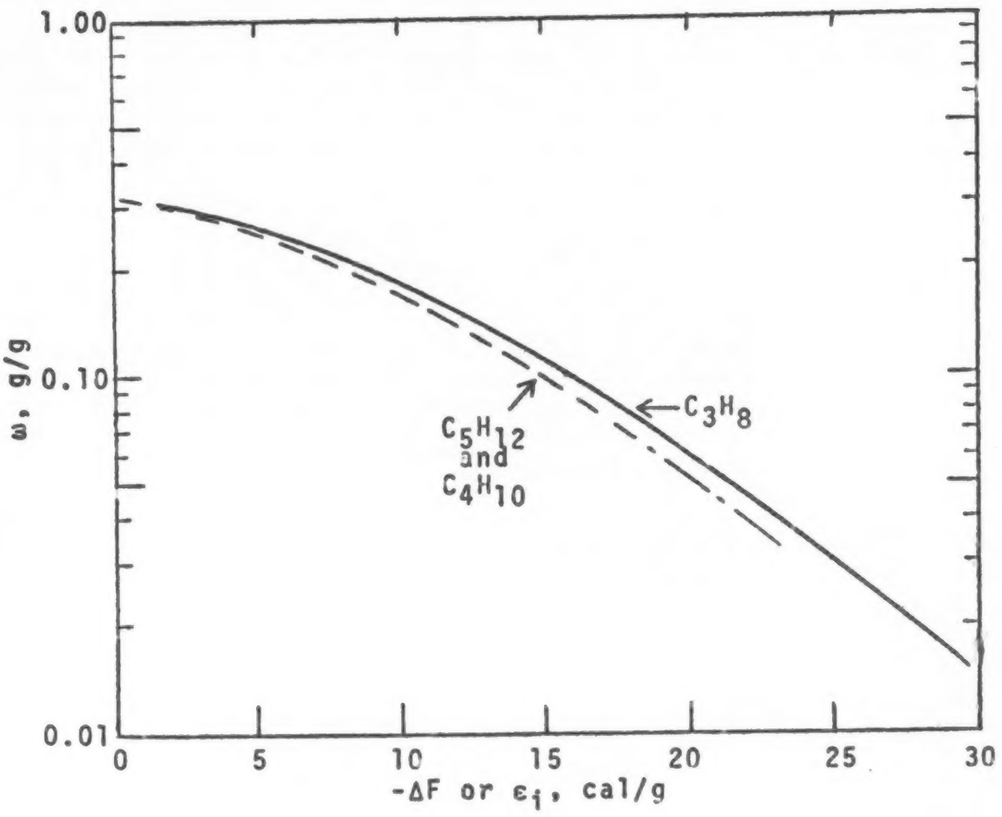


Figure 4-9 Variation of Free Energy ΔF or ε_i, with Amount of Vapor ω Adsorbed on Activated Carbon. ω, ΔF and ε_i Measured per Gram of Vapor

ordinate scale as function of the quantity 19 or 20 above on a linear abscissa scale. Whatever density is used to calculate molar volume V is also used to calculate the liquid volume of ω; the effects of density selection thereby tends to cancel out. For future reference, the quantity in 19 or 20 is designated by A when it is more convenient to do so.

The adsorption results for propane, butane and pentane as presented in Figure 4-8 are replotted in Figure 4-10, using quantity 19 and molar volume V_m as measured at the normal boiling point. ω was also converted from g/g to cm³ liq/g, using the liquid density at the normal boiling point. To obtain V_m, the method of LeBas was used; see Appendix D for table of additive volume increments.

The method gives the best generalized adsorption curves for homologous series. On activated carbons the generalized curves of different homologous series tend to coincide; the largest variance comes at the large A values. Grant, et al. found that the generalized curve for sulfur compounds was considerably above that for hydrocarbons. On silica gel the variances between curves of different homologous series are larger; adsorption data on one homologous series do not lead to an acceptable prediction regarding adsorption of members of other homologous series.

Effect of Pore Structure on Generalized Adsorption Curve - Figure 4-11 shows three generalized adsorption curves that may cover the range of this type of curve for commercial carbons suitable for vapor phase adsorption. S154 is an experimental superactivated peach pit carbon of 154% carbon tetrachloride activity having micropore volume near 1.00 cm³/g. It is similar to carbon IV of Figure 4-1 but with larger micropore volume and also larger mean micropore diameter. It approaches the upper limit on high capacity carbons. GI is a high activity coconut carbon of 0.65 cm³/g micropore volume. The generalized adsorption curve for BPL was determined with adsorption data of sulfur containing vapors such as methanethiol, ethanethiol, propanethiol, hydrogen sulfide and carbon disulfide. These vapors are more strongly adsorbed than other organic vapors of equivalent A value. Generalized adsorption curves for other carbons are expected to be below this BPL curve at the larger A values.

Figure 4-12 shows generalized adsorption curves that are typical of solvent recovery and gas mask carbons. The pore size distribution of SXA is number III in Figure 4-1 and that of the upper BPL curve is number II in Figure 4-1. The lower BPL curve, designated here as Type V, was obtained from studies carried out by Robell (1965), and is presented here because a large number of regeneration calculations discussed in Chapter 6 are based on this curve.

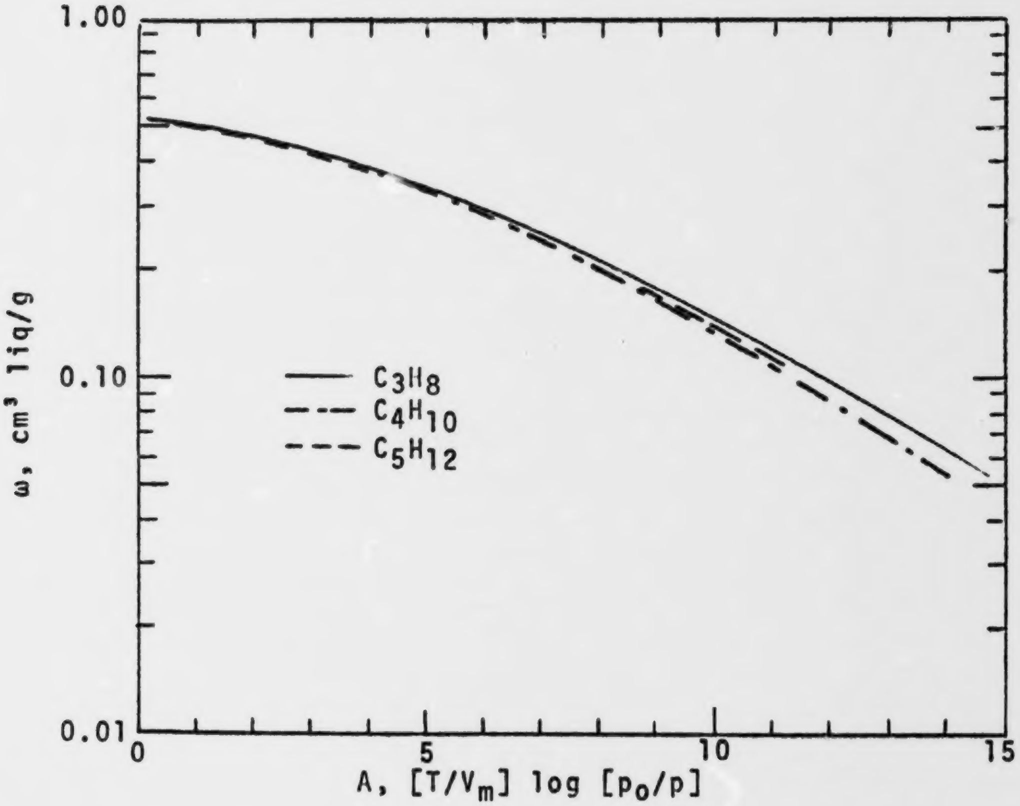


Figure 4-10 Generalized Isotherms For Propane, Butane and Pentane

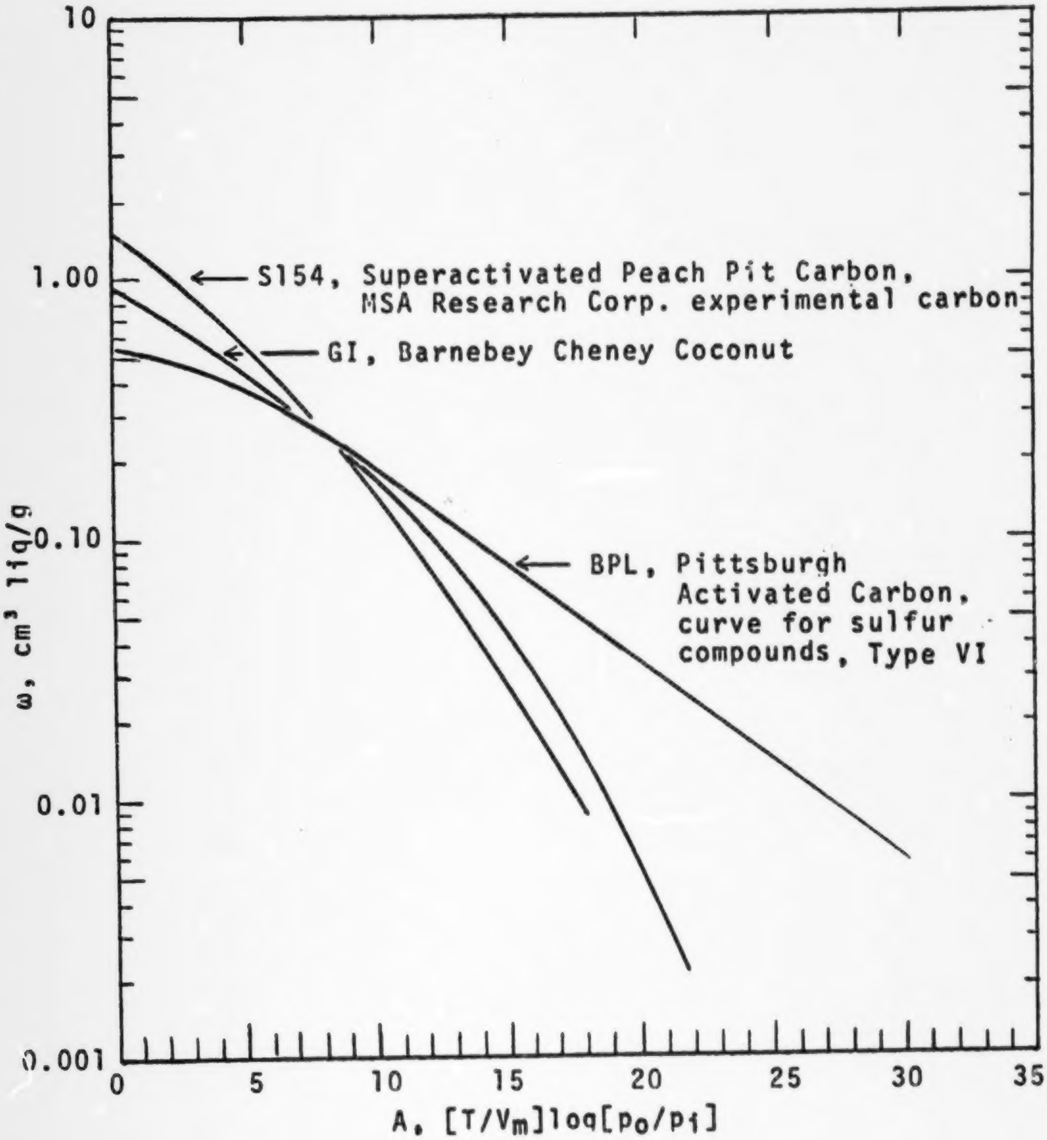


Figure 4-11 Generalized Adsorption Curves For Three Widely Different Types of Activated Carbon

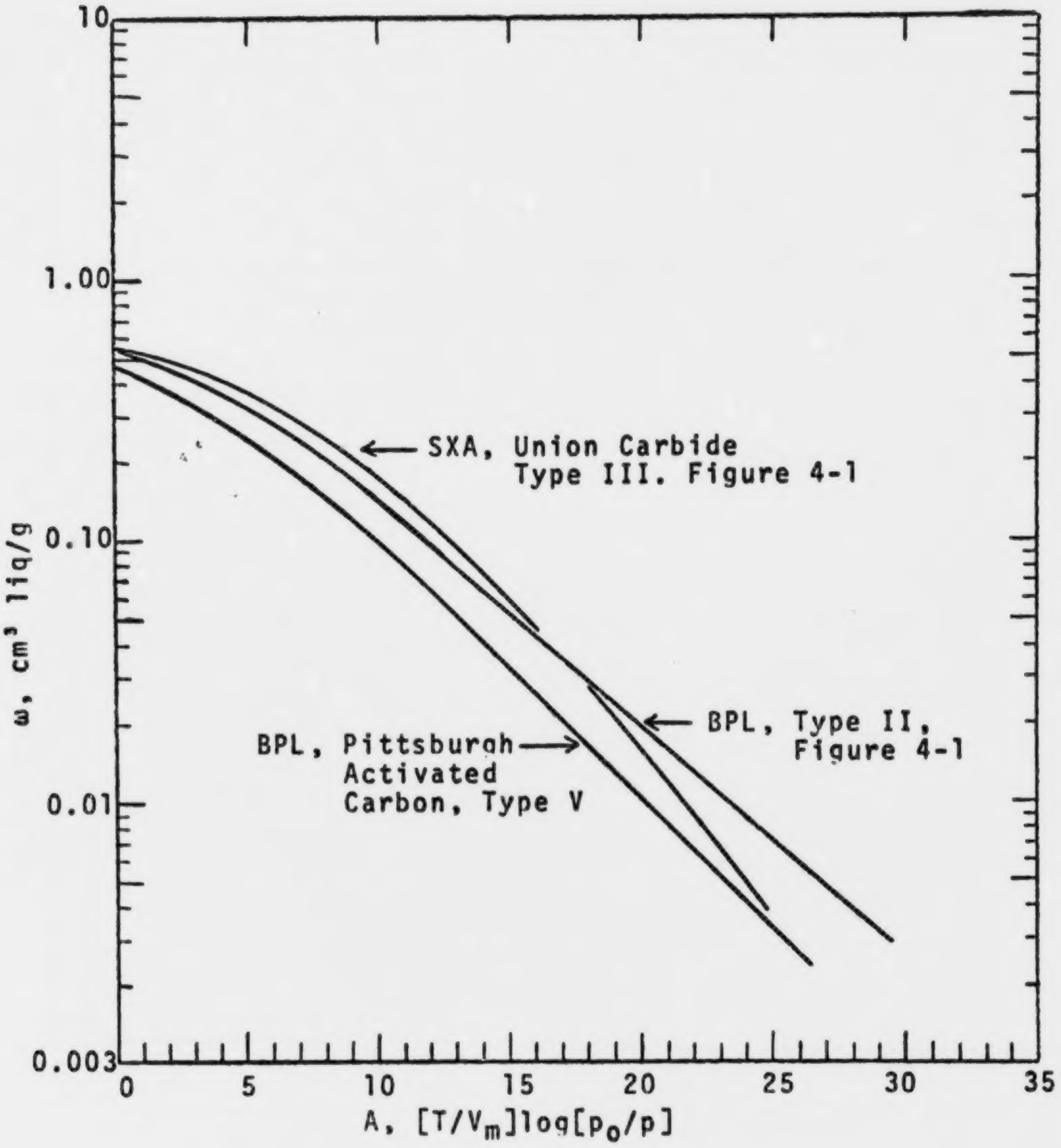


Figure 4-12 Generalized Adsorption Curves Typical of Activated Carbons Used in Gas Masks and Solvent Recovery

Under the conditions of the carbon tetrachloride activity test described in Appendix D,

$$[T/V_m] \log [p_0/p] = 2.5 . \qquad (4\text{-}21)$$

At 2.5, ω = 0.45 cm³ liq/g for BPL(II). From Curve II in Figure 4-1, ω = 0.45 cm³/g corresponds to a pore diameter of 40Å. This means that all adsorption at A larger than 2.5 occurs in pores smaller than 40 Å diameter, and also the curvature of the generalized adsorption curve is determined by the distribution of pores in this small-diameter range. For SXA Curve III, the volume of pores smaller than 40 Å diameter is 0.48 cm³/g. Above 0.05 cm³/g pore volume, the pore diameters of SXA are smaller than those of BPL. This accounts for the stronger adsorption by SXA at ω larger than 0.05 cm³ liq/g. At A = 17 or ω = 0.05 cm³ liq/g, the SXA and BPL curves cross each other; and likewise the pore-size distribution curves cross each other at 0.05 cm³/g pore volume. At ω or pore volume less than 0.05, BPL is the stronger adsorbent.

In macropores larger than 40 Å diameter or, stated otherwise, at A less than 2.5, adsorption proceeds very slowly, although for SXA and BPL the available macropore space is about 0.40 cm³/g. At A less than 2.5, ΔF, the driving force, for the adsorption approaches zero, and at the theoretical point where all the pores are filled

$$\Delta H = T\Delta S \qquad (4\text{-}22)$$

By accurate measurements of adsorption at p/p_0 above 0.99, the generalized adsorption curves of SXA and BPL would approach A = 0 gradually and stop at ω near 0.85 cm³ liq/g. By a straight extrapolation of the curves to A = 0, as done in Figure 4-11, and -12, the ω intercepted is a measure of pore volumes usually of diameter less than 100 Å.

The operating capacity in solvent recovery applications is in the low A value range (1 to 15); hence, a large adsorptive capacity is desirable in this A value range but, to ease regeneration, a low capacity is desirable in the higher A range. To adsorb weakly adsorbed pollutants or pollutants at very low concentrations, strong adsorption is required at large A values (above 15); the capacity at low A values in this case makes very little or no contribution.

Dynamic Adsorption Processes

Vapor Distribution in Adsorbent Bed - Sorption devices for solvent recovery or air purification most frequently employ a fixed adsorbent bed. It is the simplest and most trouble free in its operations. Other systems have been developed in which the adsorbent is moved countercurrent to the vapor airstream or the adsorbent is fluidized in the vapor airstream. When the adsorbent bed is fixed or moves as a unit, the vapor concentration distributions in adsorbent beds follow definite patterns that can be analyzed and the knowledge so gained used to determine the adsorbent device designs.

Curve 1 of Figure 4-13 illustrates the vapor concentration distribution at the start of the adsorption process in a fresh carbon (adsorbent) bed. The vapor concentration decreases from C_i to a concentration approaching zero in a relatively short distance. Theoretically, zero concentration is attained only at infinite bed length, but for practical purposes concentrations of 0.01 C_i to 0.001 C_i are considered essentially zero, hence the finite bed lengths.

At a later adsorption time, the vapor distribution curve has lengthened as illustrated by Curve 2. If adsorption is continued, the vapor distribution curve ultimately stops lengthening or reaches a steady state. Curve 3 shows the distribution curve when it has just attained the steady state; Curve 4 shows it when it has moved down the bed some distance in its entirety. The length of the distribution curve is the adsorption zone length, L_z. The bed length, L_s, following the adsorption zone is the saturated bed length. In this section of bed, the adsorption and desorption rates are equal; the bed is at equilibrium with the influent concentration C_i. If adsorption is continued, the adsorption zone ultimately starts to penetrate the bed as illustrated by the lower end of Curve 5. Length L_z has remained constant but L_s has increased. If it is undesirable to permit any appreciable vapor penetration, adsorption in the bed is discontinued by diverting the vapor-airflow to a fresh carbon bed. It is apparent that the full capacity of the carbon has not been utilized since L_z is only partially saturated. If it is not objectionable to allow continued and increased penetration — as when a fresh carbon bed can be connected temporarily in series with the nearly spent bed — adsorption can be continued advantageously until L_z has penetrated the bed. At this stage of the operation, the vapor concentration at the effluent end of the bed has risen to the level illustrated by Curve 6, i.e., $C_b = C_i$.

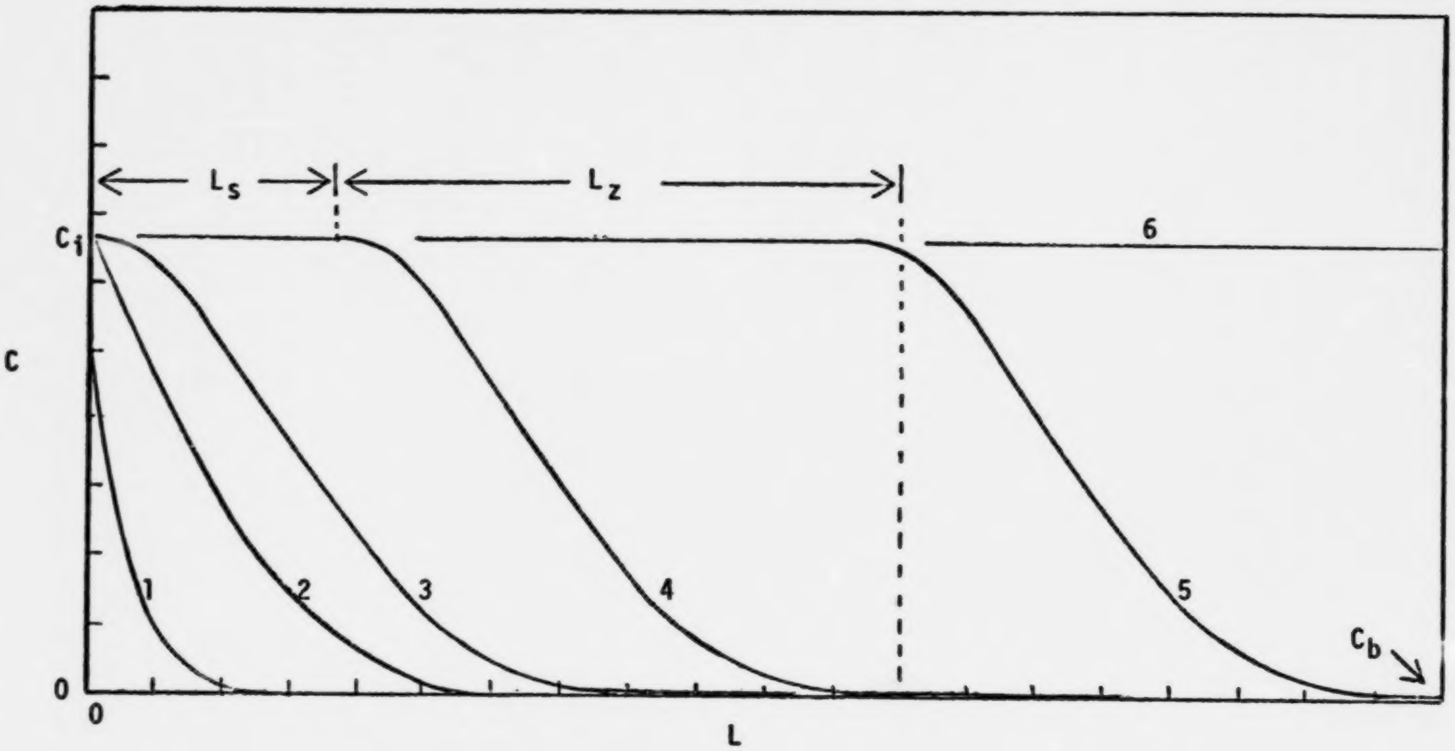


Figure 4-13 Movement of Vapor Concentration Distribution Curve in Carbon Bed With Increased Adsorption Time

As the adsorption zone depicted by Curve 5 penetrates the bed, the effluent vapor concentration changes with time in the manner shown in Figure 4-14. (This is an experimentally determined curve for butane on activated carbons; conditions of adsorption and sample calculations are given in Appendix E.) The service time, t_b, can be determined from this curve when the breakpoint concentration, C_b, is defined. The curve in Figure 4-14, indicates a service time of 600 min. at $C_b = 0.01\ C_i$ and 1100 min. at $C_b = C_i$.

In air pollutant control, the carbon bed can be operated under conditions indicated by Curves 2 to 6 inclusive. When the pollutant is strongly adsorbed, and the concentration, C_i, is very low (1 ppm) and large volumes of air are purified, the resistance to airflow becomes an overriding factor. Under these circumstances it is economical to sacrifice capacity, as when bed length is limited to those depicted by Curves 2 or 3. A short or thin bed length is used, varying from 1/2 to 2 inch, and pressure drop is maintained below 0.5 inch of H_2O. Because the concentration is low and the pollutant is strongly adsorbed, the vapor distribution curve moves down the bed very slowly. Penetration through a fresh bed may be 1% to 5%, and, after a year's time, the penetration has increased to 10%. At that time the bed is exchanged for a fresh one.

In solvent recovery the carbon bed is operated under conditions depicted by Curves 5 and 6. In these cases, C_i may be over three magnitudes larger than in odor removal, but total airflows are considerably smaller.

Determination of Service Time - To attain the desired air pollution control, or economic solvent recovery, or air purification, the service time is one of the prime factors to be considered in sizing the sorbent device.

When deep or long carbon beds are used, as in solvent recovery, L_s is large relative to L_z and essentially determines the service time. With usual solvent recovery practice, the solvent-air velocity through the bed is maintained at near 100 ft/min. In these cases L_z is of the order of 3 in. and L can range from 16 to over 36 in. The capacity of the saturated bed length, L_s, can be calculated with considerable degree of accuracy if an adsorption isotherm has been determined, or it can be estimated if a generalized adsorption curve (Figures 4-11 and -12) is available. Pollutant vapor V_m values to be used in conjunction with the generalized adsorption curves are listed in Table C-I.

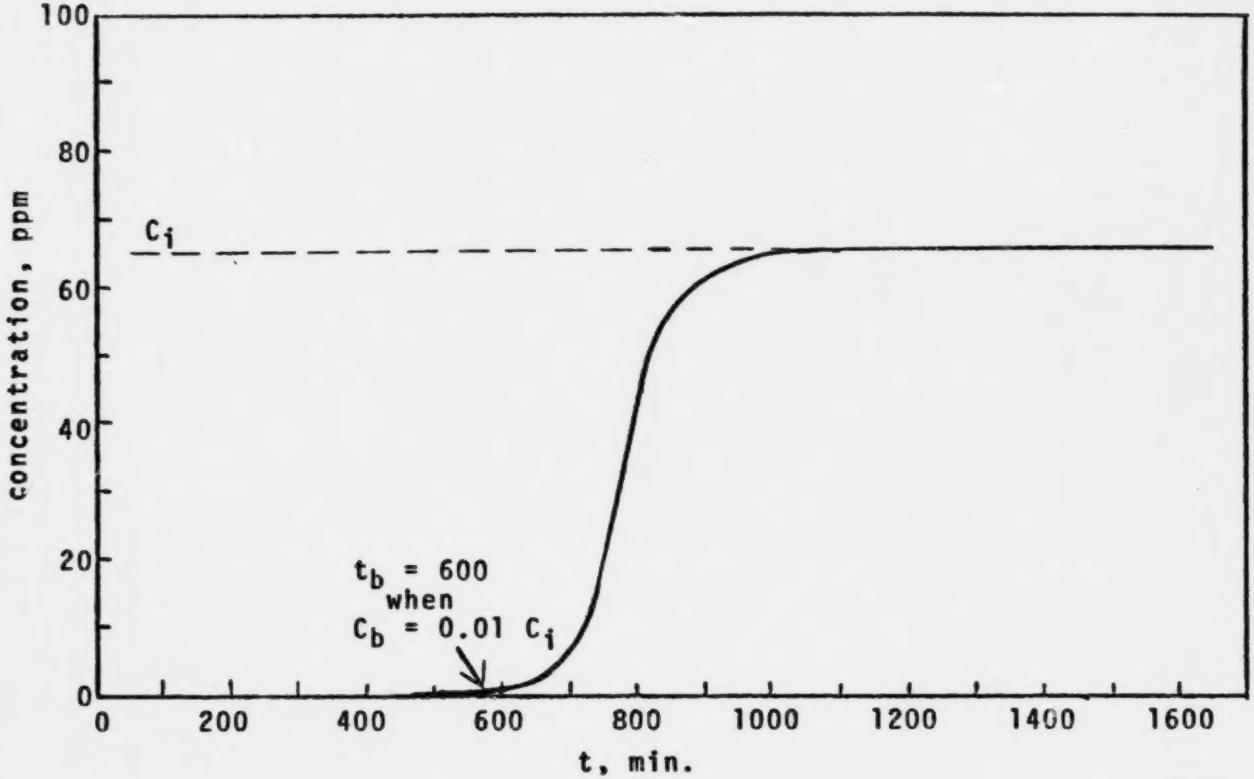


Figure 4-14 Effluent Concentration Curve of Butane Vapor From An Activated Carbon Bed as Function of Time

The capacity of the adsorption zone, besides varying with C_i and T, also varies with the carbon mesh size and flow velocity. The service time, t_b, to penetration concentration, C_b, is dependent on the saturated bed and adsorption zone adsorptive capacities as expressed by the equation,

$$t_b = \frac{A_c}{FC_i} [\omega_s L_s + \omega_z L_z], \qquad (4\text{-}23)$$

where A_c is the area of the carbon bed, F the solvent-air-flow rate, ω_s the adsorptive capacity per unit carbon bed volume in the saturated zone and ω_z the mean adsorptive capacity per unit bed volume in the adsorption zone. In this equation, $\omega_z L_z$ is a fixed amount wherein the L_z is defined as the bed length in which C decreases from C_i to essentially zero. L_s varies with the C_b/C_i ratio; at $C_b = C_i$, $L_s = L$ while at $C_b \equiv 0$, $L_s = L - L_z$.

In thin beds of 2 in. and less, as used in air purification, flow velocities near 40 ft/min. are usually employed which shortens L_z down to the 2 in. level. In these applications, the service time is essentially

$$t_b = \frac{A_c}{FC_i} \omega_z L_z \ . \qquad (4\text{-}24)$$

To attain the desired service time, the dimensions of the carbon volumes

$$A_c [L_s + L_z] \text{ or } A_c L_z$$

are optimized with consideration given to resistance to airflow that can be tolerated and the hardware to contain the carbon bed. When dealing with cylindrical beds, the parameter L/D is frequently referred to.

Characteristics of the Adsorption Zone - The adsorptive capacity and length of the adsorption zone can be calculated if the effluent concentration curve has been determined for the flow system. This is possible only if the adsorption zone has reached a steady state before the vapors penetrate the bed. If the bed is shorter than L_z, the vapor distribution curve is still changing, and the effluent concentration curve reflects this change. By procedures and sample calculations given in Appendix E, page E-5, the effluent concentration curve of Figure 4-14 was converted to the vapor distribution curve given in Figure 4-15. At C_i = 66.8 ppm, P = 5 lb/in^2 absolute, T = 111°F, 28 to 60 carbon mesh size, and 14.5 ft/min. face velocity, the following values were calculated for

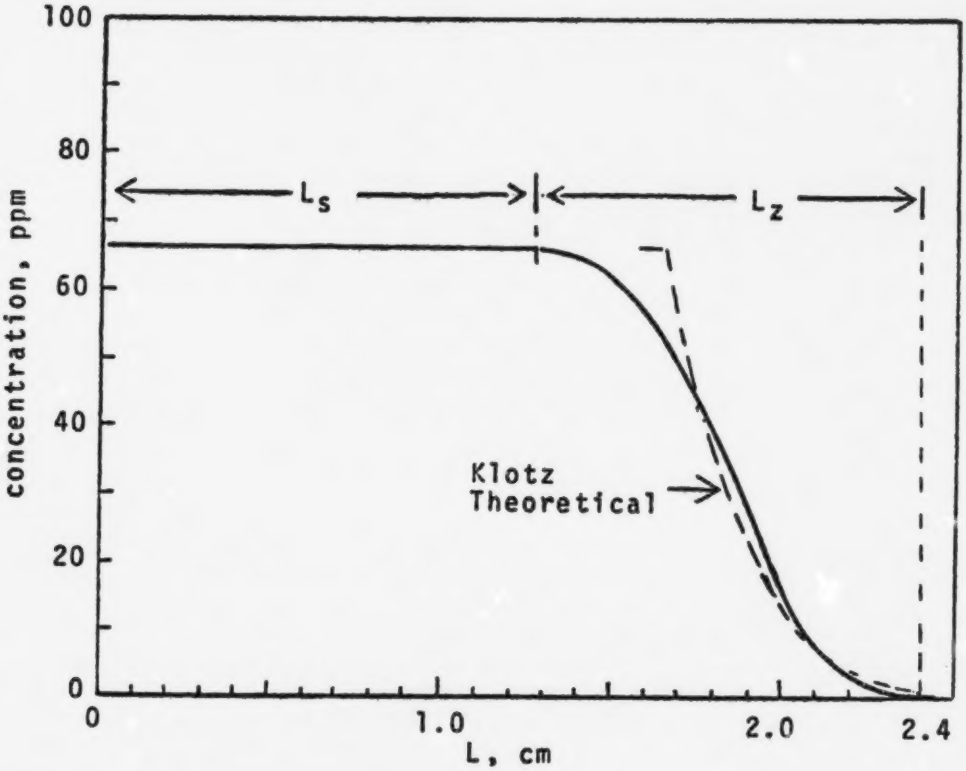


Figure 4-15 Butane Vapor Distribution in Activated Carbon Bed at Time When Vapor Has Started to Penetrate Bed

the unknown parameters of Equation 4-23:

L_s = 1.27 cm
ω_s = 0.00738 g/cm³; 0.0182 g/g
L_z = 1.13 cm
ω_z = 0.00363 g/cm³; 0.0089 g/g

$A_c\omega_sL_s$ = 0.00470 g
$A_c\omega_zL_z$ = 0.00206 g

ω_z is about one-half as large as ω_s, and on comparing the last two items about one-third of the service time for this particular vapor-adsorbent system is contributed by the adsorption zone. Since $A_c\omega_zL_z$ stays constant, all of the adsorption would occur in the adsorption zone if the bed were shortened to 1.13 cm and the service time would be reduced to 180 from the 600 min. On lengthening the bed, an increasingly larger portion of vapor will be adsorbed in the $A_c\omega_sL_s$ bed. At higher gas velocities and with coarser mesh carbons, L_z increases in length.

Critical Bed Depth - A useful concept for determining the extra amount of carbon required to accommodate the adsorption zone is the critical bed depth. This concept was first expressed by Mecklenburg (1925) in the following service time - bed length equation,

$$t_b = \frac{\omega_s A_c}{FC_i} [L - L_c] \tag{4-25}$$

where L_c is the critical bed depth. When experimentally determined t_b are plotted against L, a graph of the type shown by ABC in Figure 4-16 is obtained. At short bed lengths the graph is curved as indicated from L = 0 to some point B, and from B to longer bed lengths the graph is straight. When the straight portion is extrapolated to $t_b = 0$, it intercepts the L axis at some point now referred to as L_c. When t_b is determined at low penetration concentrations, i.e., $C_b = 0.01 C_i$, L_c is positive, when t_b is determined at C_b near $0.5 C_i$, $L_c = 0$ and at $C_b = C_i$, L_c has a negative value. Equation 4-25 has utility in adsorbent bed size, A_cL, determinations at any penetration concentration although the most frequent interest is at $C_b \cong 0.01 C_i$. An estimate of ω_s as a function of C_i is obtainable if a generalized adsorption curve is available by procedures discussed under Potential Theory Equations. L_c varies with the air velocity, F/A_c; hence, t_b must be known for one L at each F/A_c of interest as the minimum data requirement to use the equation.

The particular service time - bed length graphs in

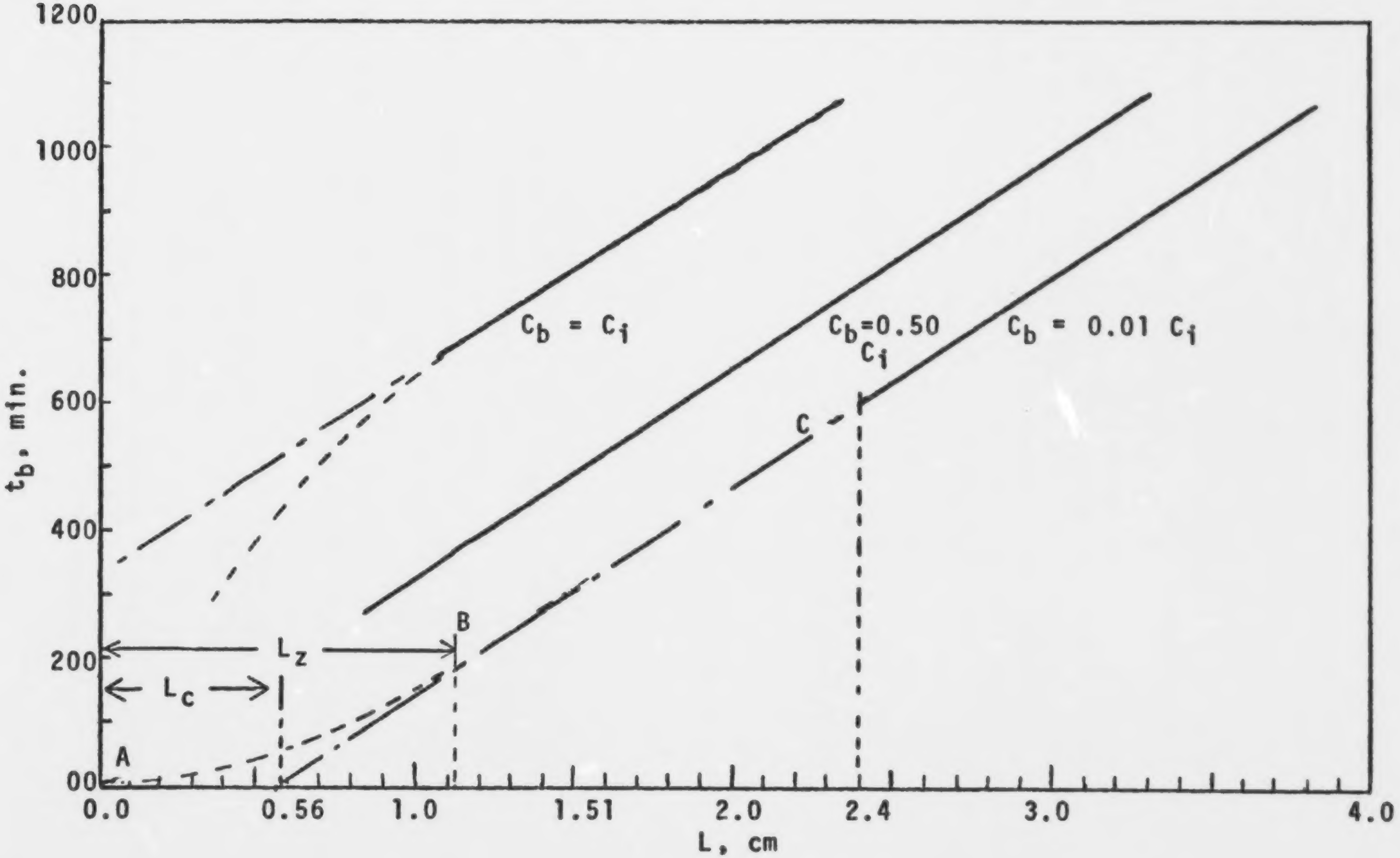


Figure 4-16 Service Time - Bed Length Curve For Adsorption of Butane on Activated Carbon

Figure 4-16 were determined from data derived from the effluent concentration curve in Figure 4-14 and data given in Appendix E, i.e., at $L = 2.4$ cm, $t_b = 600$ min, $F = 0.223$ ℓ/min, $C_i = 5.06 \times 10^{-5}$ g/ℓ, $\omega_s = 0.00738$ g/cm³ and $A_c = 0.502$ cm². L_c as calculated with Equation 4-25 and by extrapolation in Figure 4-16 is 0.57 cm.

A relationship exists between L_z and L_c which makes it possible to calculate L_c from L_z, if L_z and the shape of its vapor concentration curve happens to be known. For low C_b, i.e., when very little vapor penetration has occurred and L_z is also measured to the same C_b, the following relationship holds with which L_c can be calculated:

$$[\omega_s - \omega_z] A_c L_z = \omega_s A_c L_c$$

or

$$L_c = \left[\frac{\omega_s - \omega_z}{\omega_s}\right] L_z \qquad (4\text{-}26)$$

The quantity $\omega_s A_c L_c$ is the residual adsorptive capacity in the adsorption zone. The ratio

$$\frac{\omega_s - \omega_z}{\omega_s}$$

is readily determined from the vapor concentration distribution curve of the adsorption zone since it is the ratio of the area above the curve over the total area under C_i.

The above values of ω_s, ω_z, L_z, substituted into Equation 4-26, also yields 0.57 cm for L_c.

If C_b is large but L_z is still determined to a very low concentration, Equation 4-26 has an added term as given below,

$$L_c = \left[\frac{\omega_s - \omega_z}{\omega_s}\right] L_z - \frac{C_i F f [t_b - t_1]}{\omega_s A_c} \qquad (4\text{-}27)$$

The time interval $[t_b - t_1]$, when referred to the effluent concentration curve, is used to determine the C_b/C_i corresponding to each calculated L_c. Time t_1 is at $C_b = 0.01\ C_i$ or 0.66 ppm. The results of these calculations are summarized in Table 4-XIII; the steps performed in the calculations are recorded in Appendix E, page E-8.

If Equation 4-26 were used at C_b/C_i over 0.01, the calculated L_c would be considerably larger than the correct L_c.

Table 4-XIII L_c Calculated from L_z Using Equation 4-27

C_b	C_b/C_i	L_c, cm
0.7	0.01	0.57
1.3	0.02	0.49
4.0	0.06	0.34
11.3	0.17	0.19
27.2	0.41	0.04
33.2	0.50	-0.01

Klotz Equation - Klotz did theoretical studies to establish a relationship between the vapor concentration distribution in the adsorption zone and the physical properties of the gas and carbon. The equation involves two parts:

$$L_z = L_t + L_r \tag{4-28}$$

L_t is a function of the diffusion rate (mass transfer rate) of the vapor from the gas stream to the exterior surface of the carbon particles. The equation consists of known variables and has the form

$$L_t = \frac{2.30}{a}\left[\frac{D_p U_m \rho}{\mu}\right]^{0.41}\left[\frac{\mu}{\rho D_v}\right]^{0.67} \log[C_i/C_b]. \tag{4-29}$$

L_r is the function of processes occurring within the carbon, such as diffusion rate of the vapor molecules along the pore surfaces, accommodation of the molecules in the pores and chemical reactions. A factor that can affect both parts is the heat of adsorption, which can produce considerable rise in the carbon temperature. While the adsorption is proceeding at its maximum rate, the increased temperature reduces the adsorptive capacity, but, after the rate has subsided, the capacity increases with the falling temperature. The overall effect is a lengthening of the adsorption zone.

L_r has not been mathematically related to the properties of the system but has been found to vary linearly with the air velocity. The equation has the following form

$$L_r = 2.30\ k\ U_m \log\ [C_i/C_b] \tag{4-30}$$

Experimentally, it has been found that L_t is very small for the smaller molecules of low boiling points while L_r is relatively large. For example, L_t for the preceeding butane adsorption is 0.08 cm, while L_z is 1.13 cm. L_r, by difference, is then 1.05 cm. Therefore, the equation (4-28) has no utility for predicting L_z of the low V_m vapors. For vapors of large V_m when adsorbed on coarse mesh carbons at high vapor-air velocities, the mass transfer becomes rate controlling, and L_z is nearly equal to L_t.

The shape of the vapor concentration distribution is determined by log (C_i/C_b), as C_b is varied from essentially zero to C_i. For these curves

$$\frac{C_i\,X - \sum_{C_b}^{C_i} \Delta X\,\bar{\tau}}{C_i X} = \left[\frac{\omega_s - \omega_z}{\omega_s}\right]$$

where $X = \log\,[C_i/C_b]$. At $C_b/C_i = 0.1$, 0.01 and 0.001, the values for the above factors are 0.61, 0.77 and 0.85 respectively. For the above discussed butane adsorption, the factor at $C_b/C_i = 0.01$ is 0.50, considerably below the theoretical 0.77. This difference is due to the fact that the Klotz' theoretical curve, as shown by the broken line curve in Figure 4-15, is not sigmoid as is the one for the butane adsorption. The Klotz' theoretical shape curve is, however, frequently observed in the adsorption of higher molecular weight vapors.

Equation 4-29 gives a good measure of the effects various operating parameters have on L_t. The effects produced by the parameters are:

1. Effect of particle diameter, D_p, cm

$$L_t = k\,\frac{1}{a}\,D_p^{0.41} = k\,\frac{D_p^{1.41}}{[1-\varepsilon]6} \qquad (4\text{-}31)$$

where $a = \frac{[1-\varepsilon]6}{D_p}$. L_t increases rapidly with increased D_p.

2. Effect of vapor-air velocity, U_m, cm/sec

$$L_t = k_2\,U_m^{0.41} = k_2\,1.03\,U^{0.41} \qquad (4\text{-}32)$$

where U_m is the interparticle velocity in cm/sec and U is the face velocity in ft/min.

3. Effect of Temperature

$$L_t = k_3\,\mu^{0.26}\,\rho^{-0.67}\,D_v^{-0.67} \qquad (4\text{-}33)$$

The parameters produce opposing effects on L_t, but the overall effect is a decrease in L_t with increased temperature; μ increases with temperature while ρ decreases, both producing an increase in L_t. D_v increases with a rise in temperature producing a decrease in L_t.

4. Effect of Pressure

$$L_t = k_4\ \rho^{-0.67} D_v^{-0.67} \tag{4-34}$$

An increase in total pressure decreases ρ and D_v, thereby increasing L_t.

5. Effect of molecular size, V cm³/mol

$$L_t = k_5\ D_v^{-0.67} \tag{4-35}$$

The molecular size of the vapor affects only the coefficient of diffusion D_v. D_v decreases with increase in molecular size; hence, L_t increases.

Figure 4-17 presents three sets of curves which give L_z in inches as a function of U measured in ft/min as calculated with the complete Klotz Equation 4-28. In the figure, D_p = 0.35 cm is the mean particle diameter for 4 to 10 mesh carbon, D_p = 0.24 cm for 6 to 16 mesh and D_p = 0.12 for 12 to 30 mesh. V is the molar volume determined at 77°F. The span, including the 160, 110 and 60 cm³/mol V, covers the molecular size range of pollutant vapors of interest. The calculations were made for adsorption at 77°F and C_b/C_i was set at 0.01.

In order to use the equation for L_r, a numerical value was required for k. In studies performed for NASA under Lockheed Subcontract 28-5175, it was observed that k varies with the vapor pressure of the liquid. For pollutant vapors of interest, an average value for k is 0.008. The contribution of L_r to L_z is small; hence, the accuracy of the numerical value of k is not significant.

When all fixed quantities are substituted into Equation 4-28, the equation has the form

$$L_z = 0.80\ D_p^{1.41}\ U^{0.41}[1/D_v]^{0.67} + 0.016\ U \tag{4-36}$$

To get approximate values for D_v, Equation 10.34, page 421 from Jost (1960) was used. When all necessary constants or parameters for air are substituted into the equation, it has the reduced form

$$D_v = 7.26\ \frac{1}{[\sigma_1 + 4.18]^2}\left[\frac{M_1 + 29.2}{M_1}\right]^{1/2} \tag{4-37}$$

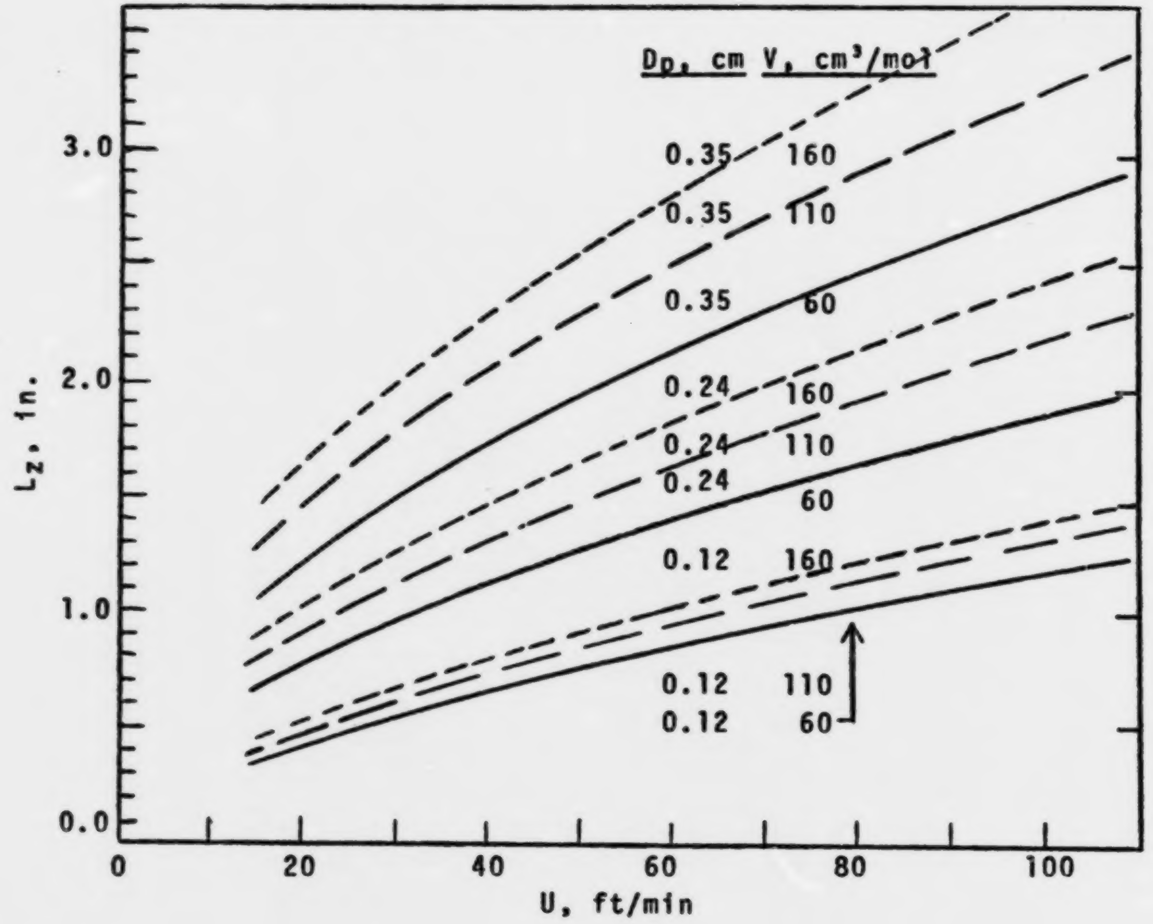


Figure 4-17 Effect of Gas Velocity, U, on Adsorption-Zone Length, L_z, for Carbons of Mean Particle Diameter, D_p, and Vapor Molar Volume, V, 4 to 10 Mesh ≅ 0.35 cm, 6 to 16 Mesh ≅ 0.24 cm and 12 to 20 Mesh ≅ 0.12 cm.

where M_1 is the molecular weight of the pollutant and σ is the collision diameter of the pollutant molecule. σ_1 is proportional to V as expressed by the equation

$$\sigma_1 = 1.328\ V^{1/3}. \qquad (4\text{-}38)$$

Table 4-XIV gives V and D_v values for some of the most frequently encountered pollutant or solvent vapors. Equation 4-37 is a function of $T^{1/2}$; 298°K has already been substituted.

Details of the procedure for calculating L_z are given in Appendix E, page E-10.

The curves in Figure 4-17 show that for the 4 to 10 mesh carbons, L_z is longer than 2 inches at U over 40 ft/min. Since coarse mesh carbons are used in thin beds, velocities are maintained below 40 ft/min to avoid too great a loss of capacity. Since the factor

$$\left[\frac{\omega_s - \omega_z}{\omega_s}\right] = 0.77$$

when $C_b/C_i = 0.01$, ω_z can be readily calculated if ω_s is known.

Table 4-XIV V and D_v for Frequently Encountered Pollutants and Solvent Vapors

Vapor	V, cm³/mol	D_v, cm²/sec
Octane	163	0.062
1,1, 3 Trimethyl cyclohexane	153	0.063
3-Methylbutyl acetate	150	0.063
4-Methyl-2-pentanone	124	0.070
Toluene	106	0.075
Pentane	114	0.078
Ethyl acetate	98	0.079
Phenol	88	0.081
Nitropropane	87	0.083
Propanone	73	0.094
Ethanol	58	0.107
Tetrachloroethene	102	0.073
1,1,1 Trichloroethane	98	0.075
Trichloroethene	98	0.077
Dichloromethane	64	0.094

Adsorption of Vapor Mixtures

The theoretical treatment of the adsorption process in the prior text of this chapter deals with adsorption of a single vapor. In actual practice, the gas phase invariably consists of two or more components; the mutual effects of the separate components requires further theoretical consideration.

The simplest system consists of a carrier gas, usually air, and the solvent (or pollutant vapor) as in degreasing and dry cleaning. Air is so poorly adsorbed relative to the solvents of concern that these gas mixtures can be considered single vapor systems as far as adsorptive capacity is concerned. This holds true with both polar and nonpolar adsorbents. However, water vapor is usually present, and in these cases the gas phase is a ternary mixture. When the adsorbent is activated carbon and the relative humidity is low, the gas mixture can again be treated as a single vapor in regard to adsortive capacity. At high relative humidities water vapor causes interference although not in the same manner as would be caused by a mixture of organic vapors. The presence or absence of water vapor is the deciding factor in the choice of adsorbents. When water vapor is present, adsorption of organic vapors cannot be effectively carried out with polar adsorbents.

In air purification and recovery of solvents used in surface coating, graphic arts, etc., mixtures of solvents are used. These solvents are strongly adsorbed relative to each other and thereby compete for the adsorptive capacity.

Displacement of Adsorbed Vapors - When an airstream containing a mixture of organic vapors is passed through an adsorbent bed, the vapors become separated along the bed length. Vapors most strongly adsorbed are separated out near the influent end of the bed and the less-strongly-adsorbed ones separate out in successive bed length segments in order of decreasing adsorbability. On continued adsorption, the more-strongly-adsorbed vapor displaces the less-strongly-adsorbed ones. The least-strongly-adsorbed vapor penetrates the bed first.

For polar adsorbents, the ranking of vapor adsorbabilities is given in Table 4-II. Water vapor heads the list, hence would displace the less polar vapors lower in the list.

For nonpolar adsorbents, the ranking of vapor adsorabilities is more dependent on polarizability or molar volume. Table C-I lists most of the pollutant vapors in decreasing order of molar volume, V_m, as measured at the normal boiling point. When there are large differences in V_m within the mixture of vapors, each vapor with the larger V_m virtually causes complete displacement of each vapor of lower V_m. When V_m are close together, displacement still occurs but is accompanied by a considerable amount of coadsorption.

Profile of Adsorbed Vapors with no Coadsorption - The profile of the adsorbed vapors in the carbon bed can be readily calculated on the basis of material balance, estimates of adsorption zone lengths from Figure 4-17 and estimates of adsorptive capacities using the potential Equation 4-19 and generalized adsorption curves of the type presented in Figure 4-11 and -12. When no coadsorption of adsorbed vapors is assumed to occur, the adsorption process is treated as though each vapor is adsorbed in a separate carbon bed but with the beds placed in series. Figure 4-18 illustrates the type of adsorbed-phase profile that is derived with this assumption for a ternary solvent mixture (Table 1-XX) used in spray coating operations.

The mixture selected for the calculations consists of 2-ethoxyethyl acetate, toluene and propanone at a total concentration of 500 ppm. This is the most probable concentration used in this operation. A 3,000 ft^3/min flow was used and bed area then sized to give a 110 ft/min air velocity. Additional parameter data for the vapor-carbon system are given in Table 4-XV. Details of the calculations are given in Appendix E, page E-12.

As shown in Figure 4-18, zones 1, 3 and 5 are saturated bed lengths. In zone 2, 2-ethoxyethyl acetate is being adsorbed while previously adsorbed toluene is completely desorbed. Similarly, in zone 4, all of the influent and desorbed toluene is adsorbed while previously adsorbed propanone is completely desorbed. In zone 6, all of the influent and desorbed propanone is being adsorbed. The zone lengths and amount of adsorption in each zone are summarized in Table 4-XVI.

By this procedure of estimating, an activated carbon bed of 63 in. diameter and 28 in. length is required to completely adsorb the ternary solvent mixture at 3,000 ft^3/min flow and 500 ppm total concentration for an 8 hr service time. The diameter becomes fixed by the flow rate and the decision to operate at 110 ft/min velocity. The bed length is determined by the type of vapors adsorbed, their concentrations, gas temperature and length of service time. This procedure is the simplest to work out but gives an overestimate of the bed length because of two factors which would have given a shorter estimated bed length had they been considered. These are (1) coadsorption occurring in both the saturated and adsorption

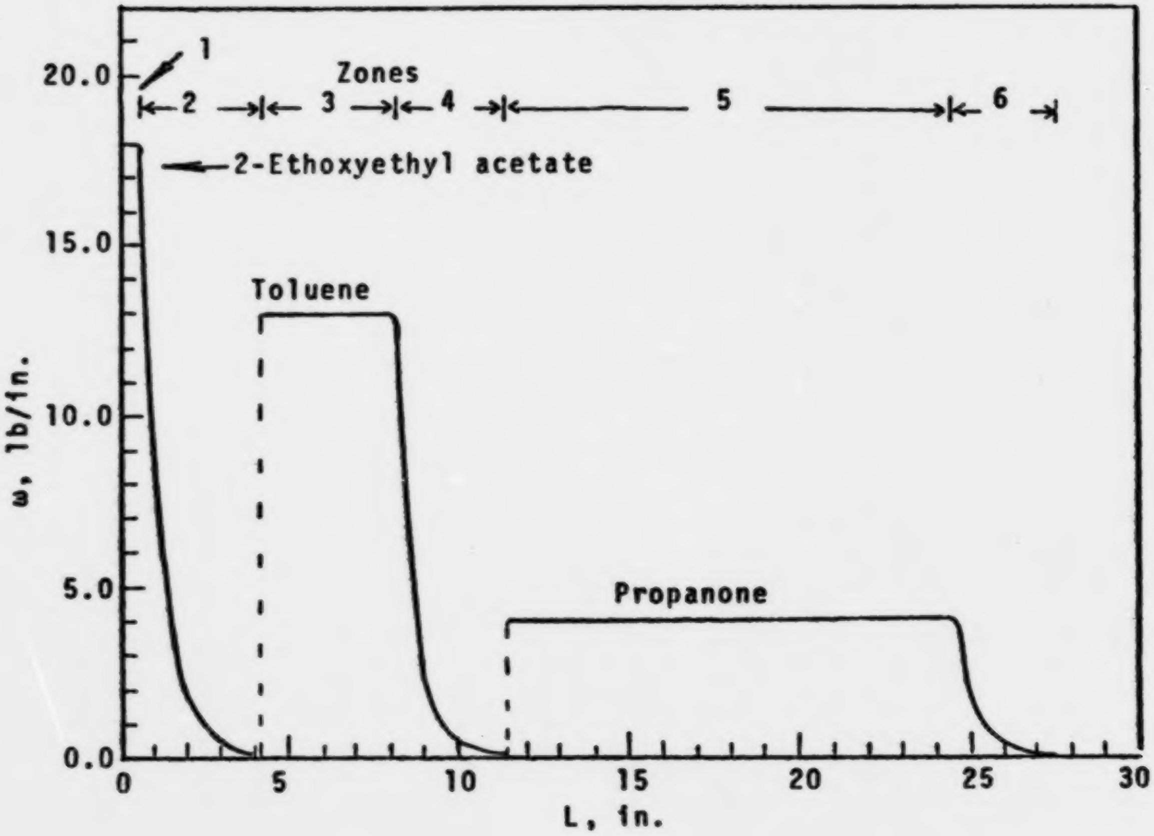


Figure 4-18 Adsorbed Vapor Profile in an Activated Carbon Bed After Steady State is Established But with no Coadsorption

Table 4-XV Selected Conditions for Adsorption of a Ternary Solvent Mixture Used in Spray Coating Operations

Total concentration, C_i - 500 ppm
2-Ethoxyethyl acetate - 50 ppm
Toluene - 181 ppm
Propanone - 268 ppm

Solvent properties	M	V$^{(1)}$	V_m	C_o,ppm
2-Ethoxyethyl acetate	132	135	163	3,400
Toluene	92	106	118	37,000
Propanone	58	73	74	290,000

Total vapor-airflow, F - 3,000 ft^3/min
Vapor-air velocity, U - 110 ft/min
Vapor-air temperature - 25 °C

Carbon bed area, A_c - 3,930 in.^{2}
Carbon particle size - 4 to 10 mesh; 0.35 cm
Carbon density - 0.50 g/cm^3; 0.0181 lb/in.^{3}
Service time, t_b - 8 hr
t_b determined at - $C_b = 0.01\ C_i$

Table 4-XVI Summary of Adsorbed-Vapor Profile Data of Figure 4-18

		L, in.	ω, lb/in.	W, lb
Zone 1, 2-Ethoxyethyl acetate	L_s	0.5		
	ω_s		17.8	
	W_s			9.4
Zone 2, 2-Ethoxyethyl acetate	L_z	3.6		
	ω_z		4.1	
	W_z			14.8
Zone 3, Toluene	L_s	4.1		
	ω_s		12.7	
	W_s			51.6
Zone 4, Toluene	L_z	3.3		
	ω_z		2.9	
	W_z			9.6
Zone 5, Propanone	L_s	13.2		
	ω_s		4.1	
	W_s			54.2

(1) Molar volume V measured at 25°C.

Table 4-XVI (Continued)

		L, in.	ω, lb/in.	W, lb
Zone 6, Propanone	L_z	2.9		
	ω_z		0.95	
	W_z			2.8
	Totals	27.6		142.4

zone bed lengths, and (2) the rise in adsorptive capacities in zones 3 and 5 because of desorption in zones 2 and 4 causing rises in vapor concentrations in zones 3 and 5. When V_m are greatly different and the adsorbed liquids are quite incompatible with each other, the estimated bed length is not too greatly in error.

Profile of Adsorbed Vapors with Coadsorption - When coadsorption and the effects of desorption are taken into consideration, the adsorbed-phase profile can be considerably different as is apparent when Figure 4-19 is compared with Figure 4-18. The zone lengths and amounts of adsorption in each zone are summarized in Table 4-XVII to permit a comparison of the results of the two procedures. Details of the calculations are given in Appendix E, page E-15.

Coadsorption is assumed to obey the following relationships between adsorption vapor pressure and mol fraction of the adsorbed phase:

For 2-Ethoxyethyl acetate[E] $C_1 = X_1 C_{o1} [\omega_t]$ (4-39)
Toluene [T] $C_2 = X_2 C_{o2} [\omega_t]$ (4-40)
Propanone [P] $C_3 = X_3 C_{o3} [\omega_t]$ (4-41)

Here C_1, C_2 and C_3 are the respective vapor concentrations or partial pressures in the carbon bed. In Zone 1 they would be the influent concentrations, but are different in the following zones. X_1, X_2 and X_3 are the respective mol fractions in the adsorbed phase. C_{o1} is the calculated equilibrium vapor pressure of E when the weight of adsorbed E is assumed equal to the sum, $[\omega_t]$, of the actual adsorbed weights of E, T and P. This is also true for C_{o2} and C_{o3}. C_1, C_2 and C_3 are known for zones 1, 3 and 5. C_{o1}, C_{o2} and C_{o3} are calculated by use of Equation 4-19 and the generalized adsorption curves of type given in Figure 4-11 . C_{o1}, C_{o2} and C_{o3} are determined at several $[\omega_t]$ until one is found that yields $X_1 + X_2 + X_3 = 1.0$. X times $[\omega_t]$ then determines the amount ω_s of each vapor adsorbed.

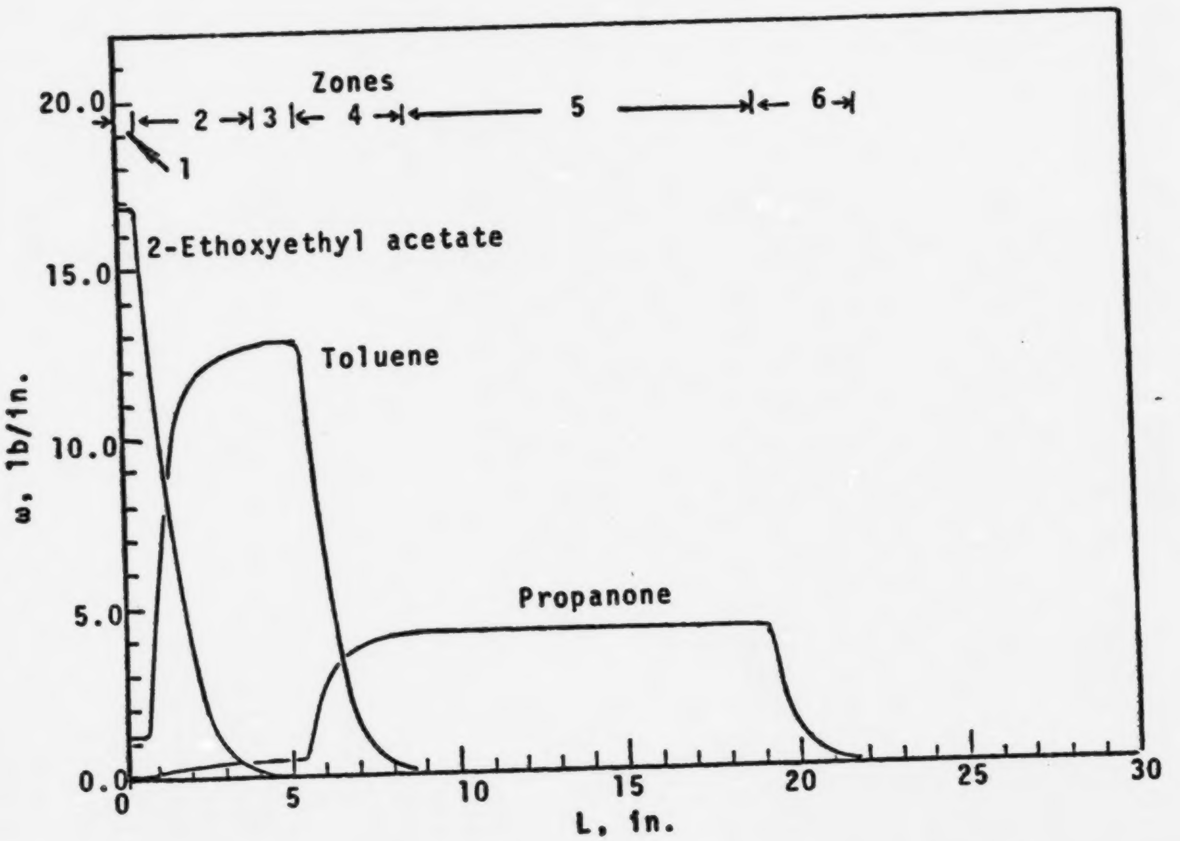


Figure 4-19 Adsorbed Vapor Profile in an Activated Carbon Bed After Steady State is Established with Coadsorption

Table 4-XVII Summary of Adsorbed-Vapor Profile Data of Figure 4-19

		L, in.	ω, lb/in.	W, lb
Zone 1	L_s	0.6		
	ω_s for E		16.9	
	ω_s for T		1.2	
	ω_s for P		0.05	
	W_s for E			10.2
	W_s for T			0.7
	W_s for P			0.03
	Total		18.1	10.9
Zone 2	L_z	3.6		
	ω_z for E, average		3.9	
	ω_z for T, average		9.86	
	ω_z for P, average		0.14	
	W_z for E			14.0
	W_z for T			35.5
	W_z for P			0.50
	Total		13.9	50.0
Zone 3	L_s	1.2		
	ω_s for T		12.8	
	ω_s for P		0.18	
	W_s for T			15.3
	W_s for P			0.22
	Total		13.0	15.5
Zone 4	L_z	3.3		
	ω_z for T average		2.95	
	ω_z for P average		3.24	
	W_z for T			9.7
	W_z for P			11.7
	Total		6.2	21.4
Zone 5	L_s	9.0		
	ω_s for P		4.6	
	W_s for P			41.5
Zone 6	L_z	2.9		
	ω_z for P		0.95	
	W_z for P			3.1
	Grand totals	20.6		142.4

The length, L_z, of zones 2, 4 and 6 are determined from Figure 4-17 and the average amount ω_z of each vapor adsorbed is determined by the factor,

$$\left[\frac{\omega_s - \omega_z}{\omega_s}\right] = 0.77$$

as worked out for Equation 4-26. The amount ω_z remaining on the carbon in zones 2 and 4 during desorption is determined by the above factor when equal to 0.23.

The procedure for carrying out the many steps of the calculation, as demonstrated in Appendix E, can be programmed and carried out rapidly by a computer when many such calculations are required.

The Equation (4-39-41) was proposed by Grant and Manes (1966). It is most accurate when applied to ideal solutions such as might be approached by homologous series. Increased deviation occurs with mixtures of dissimilar components.

The difference in bed length calculated by the two procedures is due primarily to the much larger ω_z when coadsorption is taken into consideration. Coadsorption and desorption produce a small increase in ω_s.

Under the conditions of these calculations, the coadsorption decreased the bed length from 27.6 in. to 20.6 in., or 25% decrease. When the mixture consists of very similar vapors, such as the naphthas used in surface coatings, and where the differences in V_m are small, coadsorption occurs to the greatest extent. If the service time is shortened, the L_s bed lengths decrease first and thereby the bed lengths predicted by the two procedures diverge more. Conversely, for long beds or low air velocities the predicted bed lengths converge.

Single Versus Mixture of Solvents - In surface coatings, graphic arts, rubber products and other solvent user industries, solvent mixtures are used to attain the desired viscosity, solvent power and evaporation rate of the reactant mixture. When solvent recovery is an important economic factor, consideration should be given to the possible substitution of a single solvent for the mixture. Frequently the single solvent vapor can be recovered in a smaller carbon sorbent unit. To illustrate this, carbon bed lengths were calculated to show the bed length required to adsorb each of the previously discussed solvent vapors each at 500 ppm influent concentration. As shown below, the calculated bed lengths required for single solvent vapors are compared with ternary mixtures:

Solvent	L, in.
2-Ethoxyethyl acetate, singly at 500 ppm	13
Toluene, singly at 500 ppm	14
Propanone, singly at 500 ppm	24
Ternary mixture, no coadsorption, 500 ppm	28
Ternary mixture, coadsorption, 500 ppm	21

Resistance to Airflow

An important parameter that enters into the determination of the optimum L/D ratio is the airflow resistance of the adsorbent bed. This information is generally available in the sales literature of adsorbent manufacturers, but, if not available, it can be estimated with the following equation (CEP, 1952).

$$\Delta P = L/g \left[150 \frac{(1-\varepsilon)^2}{\varepsilon^3} \frac{\mu U_m}{D_p^2} + 1.75 \frac{(1-\varepsilon)}{\varepsilon^3} \frac{G U_m}{D_p}\right] \qquad (4\text{-}42)$$

By substitution of the fixed variables for air at barometric pressure and 25°C, the equation is reduced to the form:

$$\Delta P = 2.66 \times 10^{-5} \frac{(1-\varepsilon)^2}{\varepsilon^3} \frac{U}{D_p^2} + 1.02 \times 10^{-6} \frac{(1-\varepsilon)}{\varepsilon^3} \frac{U^2}{D_p} . \qquad (4\text{-}43)$$

ΔP is in inches of water per inch of carbon bed depth, U is in ft/min and D_p in cm. The pressure drop is sensitive to the intergranular void volume fraction, ε, which varies with the way the carbon is loaded into the adsorber and with the mesh size distribution. For a tightly packed bed, ε can be as low as 0.30 and for a loosely packed bed as high as 0.45. To show the variation the tightness of packing has on ΔP, ΔP were calculated for ε between 0.30 and 0.45, when U = 40 ft/min and mesh size fraction is 6 to 16 (0.24 cm D_p). These results are as follows:

ε	ΔP, in. H_2O/in. carbon
0.30	0.51
0.35	0.28
0.40	0.18
0.45	0.10

The ΔP can vary five fold. If ε decreases due to particulate matter lodged between carbon particles, the increase in ΔP would be considerably greater.

Regeneration of Activated Carbons

The preceding text of this chapter discusses methods for analyzing the adsorption phase of the adsorption-regeneration cycle. In this part of the chapter a procedure is described for estimating the amount of regenerating agent required to regenerate a spent activated carbon. In this area considerable knowledge has been accumulated by the solvent recovery systems designers and activated carbon manufacturers. This knowledge is quite limited to operations that are profitable, i.e., concentrations generally above 1,000 ppm and recovery of the more common and more expensive solvents. Air pollution control operations, however, cover the concentration range from below 1 ppm to over 1,000 ppm and include vapors that have no recovery valve. In the concentration range 10 ppm and over, regeneration of the carbon is an economic necessity in order for the adsorption systems to be competitive with thermal incineration, catalytic incineration or liquid absorption.

When no past experience data are available, the estimating procedures for determining the carbon bed size and regenerating agent requirements perform a valuable service in regard to economic analyses and preliminary choice of type of control system best suited for the control problem under consideration.

Desorption of Adsorbed Vapors - Figure 4-20 illustrates the adsorbed-phase profile of a single vapor at the service time when the vapor has just started to penetrate the bed at some predesignated concentration C_b. This is the usual or desired status of the system just prior to regeneration. Figure 4-19 illustrates an adsorbed-phase profile for a ternary mixture. Its regeneration will follow the general pattern observed in single vapor regeneration.

Figure 4-21 illustrates the progression of the adsorbed-phase profiles as increasingly larger amounts of regenerating agent are passed through the bed in reverse flow direction. The numbers do not indicate equal time intervals nor equal amounts of regenerating agent. Adsorbed vapor at profiles numbered 1 and 2 are easily desorbed requiring relatively small amounts of agent. Increasingly larger amounts of agent are required to desorb to profiles 4, 5 and 6. With reference to the generalized adsorption curves, Figure 4-11, desorption at 1 and 2 is occurring at smaller A values, while at 6 it is occurring at larger A values. In terms of pore structure desorbed vapors at profile 1 and 2 are coming from micropores of larger diameter, while vapors at 6 are coming from micropores of small diameter. For reference, pore size distribution curves are presented in

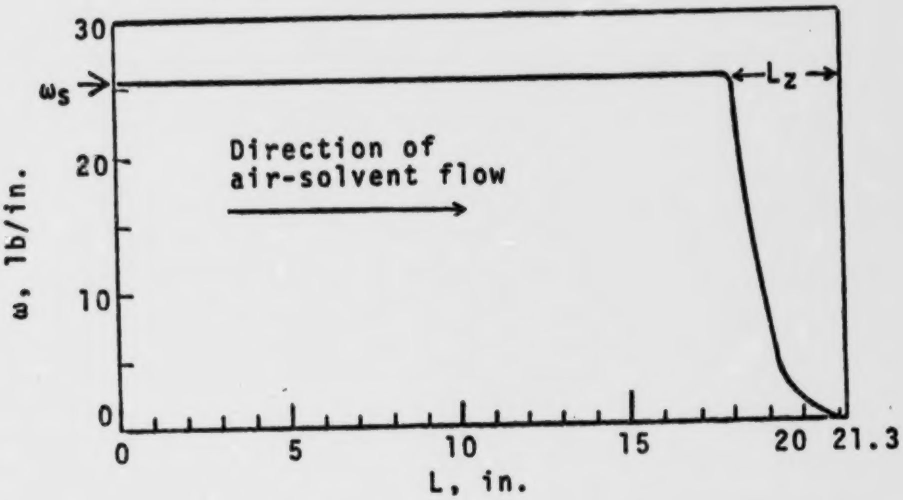


Figure 4-20 Adsorbed-Phase Profile for Trichloroethene at Service Time when Vapor Starts to Penetrate Bed, BPL V Type Carbon

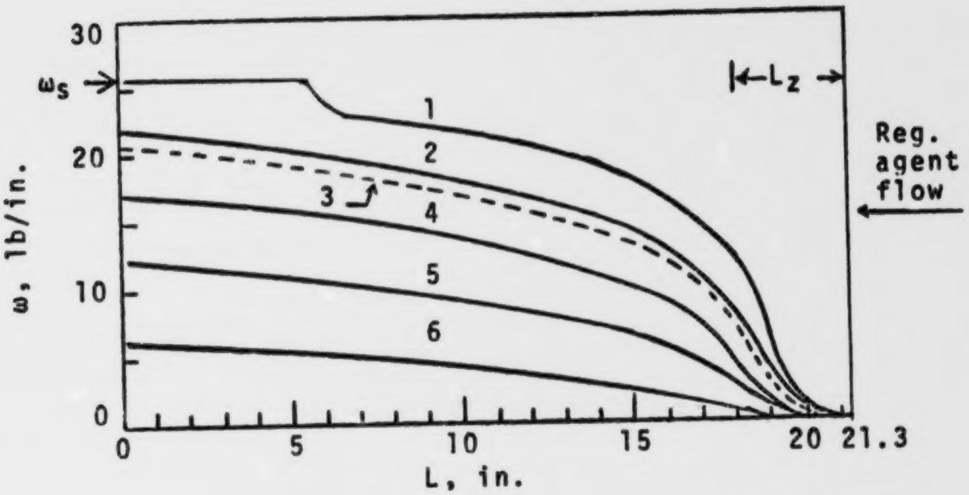


Figure 4-21 Adsorbed-Phase Profiles for Trichloroethene at Various Stages of Regeneration, BPL V Type Carbon

Figures 4-1 and -2. Very large amounts of agent are usually required to attain complete regeneration.

Procedure for Estimating Regenerating Agent Usage - A "theoretical plate" approach is used in these estimates. The carbon bed length is divided into theoretical segments with thermal and mass transfer equilibria assumed to occur in each segment as the gas mixture passes through. The hot gas mixture entering the segment imparts heat and, according to the modified Polanyi potential (4-19), i.e.,

$$[T/V_m] \log [C_o/C]$$

or as further defined

$$A = [T/V_m] \log [C_o/C], \tag{4-44}$$

the temperature rise increases the vapor pressure C. The released vapor is swept out of the segment causing an increase in A. The rise in A registers the amount of vapor desorbed. By a summation procedure the vapor transfer over successive segments is determined as a function of the input of regenerating agent.

Because of the complexity of the calculations, they are done most efficiently by computer. To illustrate the procedure and supply data for economic analyses presented in Chapter 6, regeneration calculations were done for three solvents and four carbons after equilibration at four different influent concentrations. The steps for preparing the computer programs and for carrying out the computations are described in Appendix D.

Results of Regeneration Estimates - The calculations cover steam and air as regenerating agents at the following temperatures:

Steam at 212°F
Steam at 260°F
Air at 302°F (150°C)
Air at 392°F (200°C)

The results of the air regeneration are applicable to other noncondensable gases. The three solvents investigated are,

Trichloroethene
4-Methyl-2-pentanone
Propanone

They represent a wide range of adsorbabilities, essentially bracketting most of the pollutants that are of concern. The four carbons, listed below, were chosen to represent four diverse types of generalized adsorption curves.

Barnebey Cheney GI Type, density 24 lb/ft^3
Pittsburgh BPL II, density 31 lb/ft^3
Pittsburgh BPL V
Pittsburgh BPL VI

The GI represents a highly active carbon with pore structure similar to S154, Type IV in Figure 4-1. The BPL Types II, V and VI are the same carbon, but represent different generalized adsorption curves (Figure 4-11 and -12) by different investigators on greatly different types of compounds. The Generalized Adsorption Curves II and V are representative of most vapor phase carbons.

In regard to flows and bed dimensions the following additional conditions are stipulated:

Influent flow, F	3000 ft^3/min, stp
Influent flow velocity, U	110 ft/min
Bed area, A_C	27.2 ft^2, 3930 in^2
Bed length, L	21.3 in. BPL, 23 in. GI
Adsorption-zone length, L_Z	3.3 in.
Carbon weight	1500 lb
Mesh size	4 to 10

Figures 4-22, -23 and -24 present the calculated results selected to illustrate some of the regeneration situations that can arise during pollution control operations. Each curve was calculated for a 1500 lb carbon bed (i.e., L = 21.3 in. for BPL and 23 in. for GI) that had been exposed (equilibrated) to the given concentration until the bed was saturated to its entire length. The abscissa gives the mean weight of adsorbed vapor remaining on the carbon after the amount of regenerating agent, as given on the ordinate, has passed through the bed.

Necessary data are presented in the curves to permit calculation of: (1) the total regenerating agent throughput, (2) total amount of vapor desorbed, (3) total amount of adsorbed vapor remaining on the carbon, and (4) amount of regenerating vapor required to desorb a unit weight of vapor. A typical problem would be the estimate of the required amount of 212°F steam to regenerate the carbon bed on a one-hour cycle for trichloroethene at 3,000 ppm influent concentration. From Figure 4-22, the saturation capacity is 0.363 lb solvent/lb carbon or for 1500 lb the total amount of solvent in the carbon is 545 lb. To operate on a 60 min cycle, 180 lb of the solvent must be desorbed on each regeneration leaving 365 lb on the carbon. The 365 lb gives an average 0.243 lb solvent/lb of carbon. From Figure 4-22, the amount of steam required to desorb to 0.243 is 0.30 lb/lb carbon. Total steam requirement is then 450 lb

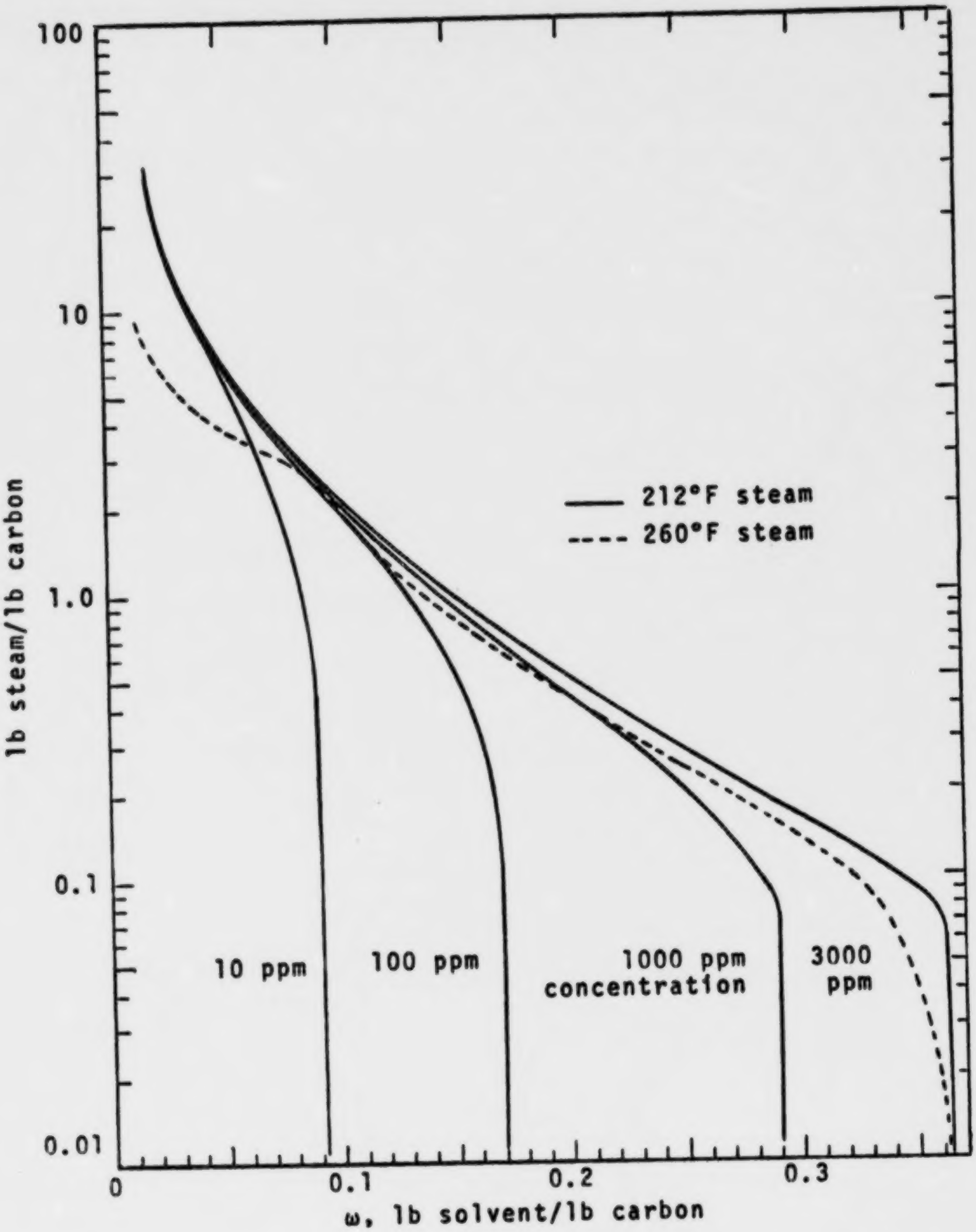


Figure 4-22 Amount of Steam Required to Regenerate BPL V Type Carbon Equilibrated with Trichloroethene at Varied Concentrations

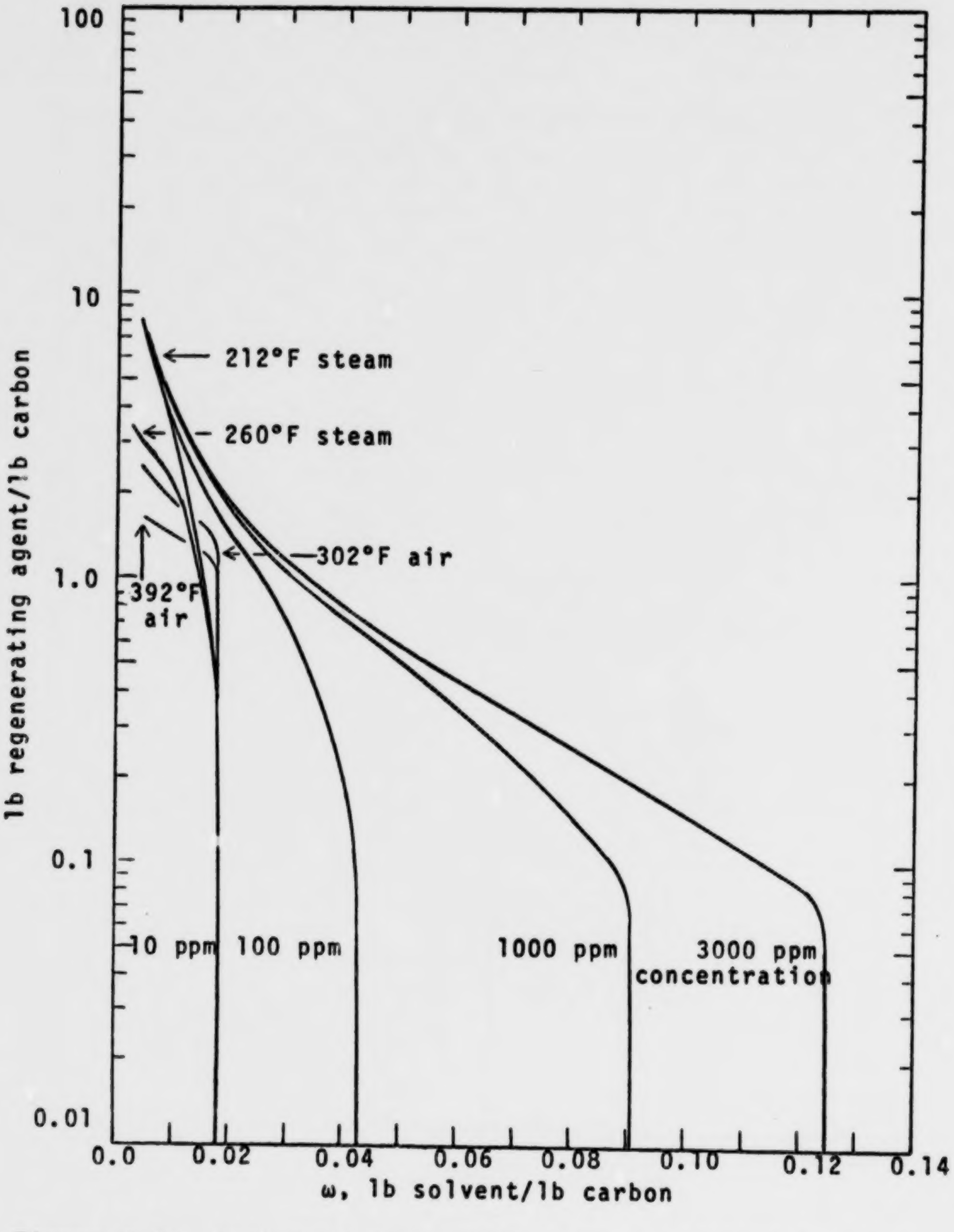


Figure 4-23 Amount of Regenerating Agent Required to Regenerate BPL V Type Carbon Equilibrated with Propanone at Varied Concentrations

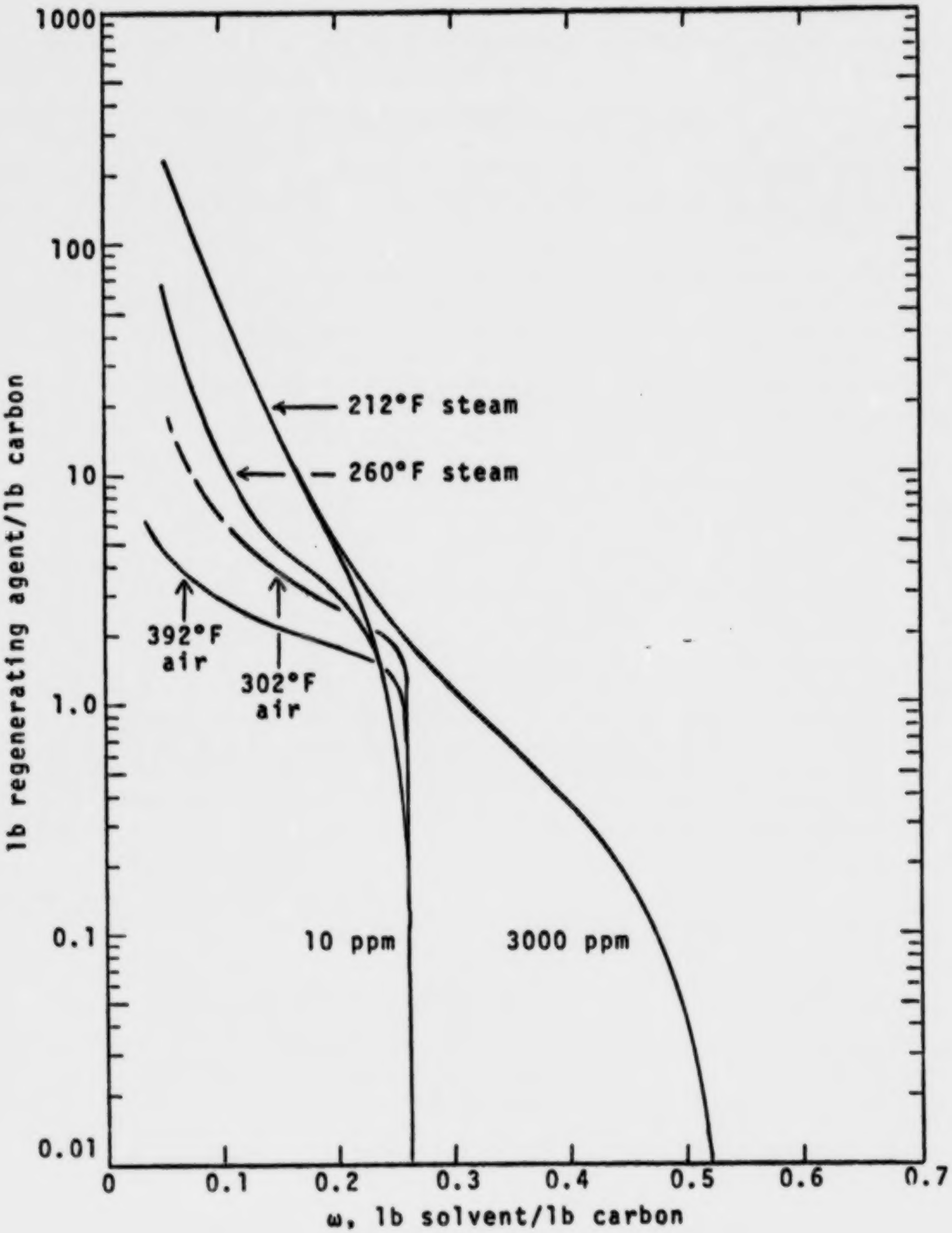


Figure 4-24 Amount of Regenerating Agent Required to Regenerate GI Type Carbon Equilibrated with 4-Methyl-2-Pentanone at 10 and 3000 ppm Concentrations

and the pounds of steam used per pound of solvent recovered are then

$$0.30/[0.363-0.243] = 2.5.$$

For deep beds of 16 to 36 in., this method gives a quick but approximate method for estimating regenerating agent requirements.

Since most solvent recovery operations are carried to service times at low vapor penetration, some adjustments are required to take into consideration the effect of the adsorption zone. This can be done by programming the adsorption zone into the computer, or it can also be estimated from the adsorbed-vapor profiles. The profiles shown in Figure 4-21 are for trichloroethene when the adsorption phase of the cycle is at 3000 ppm concentration. They were read-out when the computer was operating on the 3000 ppm curve in Figure 4-22 for 212°F steam. The computer calculated profile extends from $L = 18$ in., in reverse direction, to $L = 0$ and theoretically to $L = -3.3$ in. The parts of the profiles in L_Z are extropolations of the computer calculated curves. The effect of L_Z is that between 10 to 12 lb additional steam is required. The steam requirements for the $L = 0$ to 18 in. profiles lengths are still the same as originally calculated for $L = 21.3$ in. i.e., the efficiency of steam utilization increases as the bed length is increased. To determine the amount desorbed, the area under each profile is subtracted from the pounds adsorbed at the time of the initial penetration, i.e., when $C_b \gtrsim 0.01\ C_i$. The total pounds adsorbed comes to

$$L_S \times \omega_S + L_Z \times \omega_Z = W,$$

where $$\frac{\omega_S - \omega_Z}{\omega_S} = 0.77;\ \omega_Z = 0.23\ \omega_S$$

and $$18 \times 25.6 + 3.3 \times 0.23 \times 25.6 = \underline{480\ \text{lb}}$$

Table 4-XVIII summarizes the pertinent quantities calculated from the profiles. The general pattern as established for this solvent-adsorbent system appears in other systems. The regeneration time, as given in Column 2, is calculated for a steam flow rate of 250 ft³/min measured at standard temperature and pressure.

When L_Z is taken into consideration, 2.8 lb steam/lb solvent is required to desorb 180 lb of trichloroethene, Profile 3. The regeneration time is established at 40 min and steam requirement at 500 lb to recover the 180 lb of solvent per cycle.

Table 4-XVIII Regeneration of Trichloroethene-Activated Carbon System Based on Figure 4-21 Profiles

Profile	Regeneration time, min	Steam input, lb	Solvent desorb.,lb	Lb steam per lb solvent
1	17	210	79	2.7
2	33	410	160	2.6
3	40	500	180	2.8
4	65	810	240	3.4
5	145	1820	310	5.9
6	640	8040	410	20

Operating Capacity - An examination of Figures 4-22, -23 and -24, and the results of Table 4-XVIII show that the amount of regenerating agent required increases rapidly as desorption is carried closer to completion on each cycle. In order to maintain a profitable solvent recovery operation, the extent of desorption, now termed the operating capacity, must be closely gauged to minimize the steam-to-recovered solvent ratio. Table 4-XIX gives steam-to-solvent ratios and operating capacities for the three solvents when the vapor influent concentration is 3000 ppm and the adsorption-regeneration cycle time is one hour. Two to four pounds of steam for each pound of solvent recovered are considered optimum ratios; 4-methyl-2-pentanone and trichloroethene fall in this range with the particular sized system under discussion.

The steam-to-solvent ratio of 6.1 for propanone recovery is on the high side. It can be lowered by decreasing the operating capacity, but to do this will require an increase in bed size. There is, however, a limit to the extent the bed size can be increased since steam requirements to heat the carbon and associated hardware increase.

In these particular recovery operations the steam required to heat the bed to 212°F and supply the heat of desorption is 80 to 100 lb. This steam condenses and remains in the bed. The balance of the steam, 200 to 400 lb, serves as a sweep gas.

As the influent concentration decreases the service time increases and the amount of regenerating agent required also increases. In Table 4-XX this type calculated data are presented when the influent concentration is 10 ppm. The steam-to-solvent ratio for each vapor comes to a minimum at some operating capacity. For 4-methyl-2-pentanone the minimum is at 0.025 lb/lb operating capacity, for trichloroethene at 0.025 lb/lb and for propanone at 0.005 lb/lb. The service time in each

Table 4-XIX Estimated Operating Capacities and Steam Requirements for Recovery of Trichloroethene, 4-Methyl-2-pentanone and Propanone for a One-Hour Adsorption-Regeneration Cycle Time, Carbon Equilibrated at 3000 ppm

Solvent	V_m	Solvent desorb., lb	Steam used, lb	Lb steam per lb solvent	Operating capacity, lb/lb
4-Methyl-2-pentanone(1)	140	135	360	2.7	0.09
Trichloroethene	98	180	450	2.5	0.12
Propanone	74	80	490	6.1	0.05

(1) 4-Methyl-2-pentanone adsorbed on GI type carbon and the other two solvents on BPL V type carbon.

Table 4-XX Estimated Steam Requirements to Regenerate Carbons(1) Equilibrated with 4-Methyl-2-pentanone, Trichloroethene and Propanone at 10 ppm Influent Concentration and at Varied Operating Capacities, 212°F Steam Used

Solvent (Pollutant)	Operating cap., lb/lb	Service time, hr	Solvent desorb., lb.	Steam used, lb	Lb steam per lb solvent
4-Methyl-2-pentanone	0.01	33	15	1200	80
	0.025	82	37.5	3000	80
	0.05	163	75	9000	120
	0.16	610	---	---	--
Trichloroethene	0.01	25	15	1950	130
	0.025	62	37.5	4500	120
	0.050	125	75	12700	170
	0.092	230	---	---	--
Propanone	0.0025	14	3.75	1300	340
	0.005	28	7.5	2400	320
	0.010	56	15	5000	400
	0.014	100	---	---	--

(1) All calculations are for BPL V type carbon

case is sufficiently short so that steam regenerations, even though large amounts of steam are required, are much less costly than carbon replacement and reactivation. The longest service is for 4-methyl-2-pentanone at 0.16 lb/lb saturation capacity. The 610 hr at 24-hr days is equivalent to a one-month service time.

When the influent concentration is down to 1 ppm the pollution control operations change. At this concentration it would take about one year to equilibrate the carbon with 4-methyl-2-pentanone. The cost of steam regeneration is at the same cost level as carbon replacement and reactivation.

Selection of Regenerating Agent - As the results presented in Table 4-XX show, the amounts of steam required for regeneration are large relative to the amounts of solvent desorbed. Miscible solvents (or pollutants) as represented by 4-methyl-2-pentanone and propanone are completely dissolved in the large amount of steam condensate. Their recoveries by distillation are not economical, thereby creating a disposal problem if water pollution is to be avoided. In these cases the solution to the problem is to regenerate the carbon with a noncondensable gas and burn the released vapors immediately in a small thermal incinerator. If the amount adsorbed is small so that the release rate never exceeds 25% LEL, then air can be used as a regenerating agent; otherwise, an inert gas such as flue gas would be safer. By the procedures already demonstrated, the noncondensable agent requirements can be calculated. The cost of using noncondensable gases is lower than that of steam since no fuel is required for latent heat of vaporization.

When the condensed vapor is insoluble in the steam condensate, or slightly soluble as is trichloroethene, complete or partial separation of the organic liquid is then possible by decantation.

When the desorbed organic liquid is soluble, but on thermal incineration would repollute the air, as by release of SO_2, HCl or NO_2, the problem of pollutant disposal becomes more difficult.

At higher influent concentrations where the steam-to-solvent ratio decreases, the advantages of using noncondensable regenerating agents decrease. In the concentration range where solvent recovery is practiced, steam is the only practical regenerating agent.

Some calculations were carried out to determine the performance of 260°F steam. The general conclusions are that in the high concentration range, above 1000 ppm, it offers very little advantage over the use of 212°F steam. At times the use of 260°F steam serves a useful purpose for the periodic removal of high molecular weight molecules, which when present in the airstream, accumulate in the influent end of the carbon bed. When regeneration with 260°F steam is carried to low solvent contents, the steam condensed in the early part of the regeneration is vaporized leaving a dry carbon bed. It then behaves as a noncondensable gas but is more costly to use than air or flue gas.

Generalization on Adsorbent System - The results of the calculations on adsorption and regeneration discussed in this chapter were used to work up the costs of operating adsorbent systems. These costs were compared to those for the competing systems, thermal incineration and catalytic incinerations. A number of generalizations were arrived at in regard to the circumstances under which each system might be used advantageously. These generalizations are presented in Chapter 1, pages 20 to 24.

5. Theories and Types of Catalysts

Background

Terminology

The general characteristics of the process termed "catalysis" were outlined by Berzelius. In 1835, he codified most of the chemical reactions developed to that time and observed that many reactions were affected by the presence of a nonreacting substance. The process appeared to be initiated by a "catalytic force" which separated or broke down the reactants prior to the chemical reaction. He used the term "catalyst" to define that substance whose presence affected the rate of a reaction while remaining essentially unchanged itself.

Modern scientific technology has significantly altered the "catalytic force" concept proposed to explain catalysis. The fundamental principles of catalysis are being gradually unveiled through the combination of modern analytical instrumentation, continued research and the correlation of previous data. Mechanisms and theories describing the process of catalysis continue to evolve as the result of these investigations.

Development

Although catalytic reactions have been used for over a thousand years, theories describing these reactions have been actively developed only during the last sixty years. The works of Freundlich (1915), Langmuir (1918) and Sabatier (1920) have been used as the foundation for most of these theories. Catalysis has a dual nature involving both physical and chemical aspects which have stimulated much of the research towards a description of its complex nature.

Description

Three factors have been established as criteria for describing catalysis: (1) the catalyst remains chemically unchanged, (2) the reaction rate can be correlated to the amount of catalytic reaction surface, and (3) the catalyst does not affect the equilibrium concentrations. Examples of catalysts, which conform to these criteria, are available for solid, liquid and gaseous states, with both positive and negative influence on the chemical reaction. A concise definition and evaluation of the theories and types of catalysis can be found in Kirk-Othmers' Encyclopedia of Chemical Technology.

Air pollution control systems are almost exclusively confined to solid-gas, or heterogeneous contact catalysis. The definitions, formulae and cursory examinations of theoretical models presented in this chapter pertain to heterogeneous catalysis.

Reactions of gases at a solid catalyst surface present one of the more important alternatives available for air pollution control. However, it is necessary to understand and use some theoretical models and mechanisms to discern its prominence in pollution control systems.

Theoretical Models

Types

The prominence of surface and surface effects in heterogeneous catalysis is evident in the theoretical models developed to describe these reactions. Theories of catalysis fall into four general categories: (1) geometric, (2) electronic, (3) boundary layer and (4) crystal field. Research and development of theoretical models for catalysis have lagged behind the applications of catalysis, but have been instrumental in its recent growth.

The general idea in each of the theoretical models has been a more thorough elucidation of the "chemisorbed intermediates" proposed by Sabatier (1920). The successes attained by these various models have increased the use of catalysts and opened such fields as air pollution for their application.

Geometric

Geometric models for describing catalysis rely heavily on Langmuir's (1918) adsorption theory and surface area measurements by Emmett and Brunauer (1937) and Brunauer, Emmett and Teller (1938). Correlations between molecular or atomic volume and surface area or pore sizes were made to evaluate and predict catalytic activity.

Thiele (1938), Weisz (1954) and Wheeler (1951) did extensive work in this area. Wheeler (1955) derived the equation

$$h = \delta\sqrt{K/rD_v} \qquad (5\text{-}1)$$

to relate the reaction kinetics, pore size, surface area, catalyst specificity, apparent reaction order and poisoning. Balandin (1929) studied dehydrogenation and Beeck (1950) studied hydrogenation in relation to the geometry of various metal catalysts which engendered useful correlations.

Electronic

Dowden and Reynolds (1959) are primarily responsible for the development of the electronic theory of catalysis. Catalysts are classified as conductors, semiconductors or insulators. This theory proposes the slow transfer of electrons between catalyst and adsorbate as the rate determining step.

Boundary Layer

Recent work in catalysis has concentrated on the geometric and electronic states of surface layers only, bringing it into the realm of the boundary layer theory. The influence of surface defects, dislocations, holes and terminal surface atoms has been suggested by many researchers. These reactive centers have been used successfully to describe many types of adsorption.

Crystal Field

The partial success of electronic and boundary layer theories has been used as the basis for applying the crystal field theory. As proposed by Dowden and Wells (1961) and elaborated by Mango and Schacktschneider (1967), this theory has proven satisfactory for those few systems for which the detailed quantum mechanics of surface atoms can be calculated.

Adsorption

Description

Adsorption of gases on solid surfaces is one of the primary steps involved in catalysis. Its fundamental and unique character requires some explanation before attempting any evaluation of catalytic processes.

Heterogeneous catalysis requires at least one of the components to be adsorbed on the catalyst surface before chemical reaction can occur. This adsorption concentrates atoms at the interface between the two phases and decreases the free energy of the surface. The free energy decrease or entropy loss makes the process exothermic. The energy released during adsorption is available for the catalytic reaction (activation energy).

Theoretical Principles

Since adsorption is a basic part of catalysis, some discussion of theory is applicable. The adsorption isotherm developed by Langmuir (1918) has traditionally been used as the basis for adsorption models. His premise of kinetic and surface limiting factors has been established by many researchers. The equation is derived from the kinetic theory of gases:

$$\frac{dn}{dt} = KMS\theta, \text{ to give } \theta = \frac{KP}{1 + KP}, \text{ or} \tag{5-2}$$

$$C_A = KP_A/1 + KP_A \tag{5-3}$$

indicating that adsorption is proportional to pressure and approaches saturation at high pressures.

A more accurate representation of real systems was developed by Freundlich (1915) which has the form

$$\theta = KP^{1/n}. \tag{5-4}$$

This was shown by Taylor and Halsey (1947) to represent an adsorption in which the heat of adsorption decreases logarthmically with coverage. When the heat of absorption decreases linearly with coverage, the Temkin (1949) isotherm results.

$$\theta = A \ln Bp. \tag{5-5}$$

Application

Publications by Hinshelwood (1928) and Corrigan (1954) have shown these equations are useful in the deduction of kinetic equations. Their import is more fully realized in the determination of mechanisms for catalytic reactions. Measurements on the adsorbed "intermediates" can only be done indirectly, and these equations provide a valuable tool for the elucidation of reaction mechanisms.

System Design Theory

Approaches

Both reaction rate and thermal calculations can be used to approximate the operating parameters for catalytic purification systems. These mathematical descriptions can also be used to identify the influence of these various parameters and suggest ways to obtain optimum efficiencies.

Reaction Rates

The acquisition and interpretation of experimental data for catalyzed systems have been reviewed by several authors. Hougen and Watson (1943) developed mathematical expressions to describe catalytic reaction mechanisms. Yang and Hougen (1950) presented a summary of experimental methods and mathematical expressions for determining rates and mechanisms. Similar work has been reported by Corrigan (1954), Hwang and Parravano (1967), Otake, Kumigita and Nakao (1967) and Lin (1969). Brodski et al. (1967) have also discussed methods for determining the accuracy of theoretical mechanisms on the basis of kinetic data.

Mathematical descriptions of reaction rates have been developed empirically by Arrhenius:

$$K = A \exp \frac{\Delta E}{RT} \qquad (5\text{-}6)$$

and from statistical mechanics by Eyring:

$$K = A \frac{RT}{Nh} \exp \frac{\Delta S^{\ddagger}}{R} \exp \frac{-\Delta H^{\ddagger}}{RT}. \qquad (5\text{-}7)$$

The accuracy of these absolute reaction rates can always be improved by more complex notations involving more constants and requiring sophisticated mathematical treatment.

The general results obtained from these equations present an interesting paradox in the evaluation of catalytic systems. If these equations are used to calculate the ratio of heterogeneous and homogeneous reaction rates, the catalytic reaction rate appears considerably smaller. By making similar assumptions in the calculations of reaction rates, it can be shown that the ratio

$$\frac{K_{\text{heterogeneous}}}{K_{\text{homogeneous}}} \approx 10^{-10} \text{ to } 10^{-15} \exp \Delta E/RT.$$

In actual practice this theoretical deficit is surmounted by the decrease in activation energy and the use of large surface area catalysts. This ratio denotes the significance of the relative activation energies for catalyzed and uncatalyzed reactions. It follows, therefore, that catalysts which strongly adsorb the reacting species perform best.

Extraneous interferences may occur in three areas which render these rate calculations inoperable for some applications of catalysis. Reaction chains, extraneous chemical interactions and catalyst attrition affect the reaction rates but do not conform to simple time functions.

Thermodynamics

Thermal calculations require data from four general areas: (1) heats of reaction, (2) heat transfer coefficients, (3) reaction rates and (4) thermal properties of system. These data permit the calculation of heat release as a function of the catalytic reaction.

A volumetric heat release, for the reaction in the catalyst bed, can be described as:

$$q/V_{cat} \propto K, Q, t, P_{pollutants} \qquad (5\text{-}8)$$

Hlavacek (1970), Wilhelm, Johnson and Acton (1943) and Lin (1969) have published different mathematical solutions to this proportionality.

By assuming isothermality over small integrated sections and a linear variation of the reaction rate, Wilhelm, Johnson and Acton (1943) have generated the equation:

$$q = \int_0^r [H_o + H_1 T][2\pi r \Delta l]dr \qquad (5\text{-}9)$$

for small, cylindrical sections of the catalyst bed. In this calculation, H_o is the value (q/V_{cat}) for the initial reaction of the "clean" catalyst in equation (5-8). H_1 is the rate of change of (q/V_{cat}) as the catalytic reaction progresses; r is the radius of the catalyst bed and Δl is an incremental length.

Heat is lost from these sections of the catalyst by two mechanisms: (1) radial conduction equal to

$$-2\pi r \Delta \ell K[dT/dr],$$

where K is the thermal conductivity, and (2) volumetric convection equal to

$$2\pi r \Delta \ell K_f[T_{solid} - T_{gas}]dr,$$

where K_f is the film heat transfer coefficient.

Equating the heat generated and lost through this cylindrical section generates the identity:

$$\int_0^r [H_o + H_1 T][2\pi r \Delta \ell]dr =$$

$$-2\pi r \Delta \ell \ K \frac{dT}{dr} + \int_0^r 2\pi r \Delta l \ K_f \ (T_{solid} - T_{gas})dr \qquad (5\text{-}10)$$

Equation (5-10) may be used to describe any thermal change occurring in the system.

Solutions to these general equations form a series of curves or parabolas depending upon the system parameters. If appropriate data are available for the system, solutions can be obtained for the rate of heat release and reaction temperature. Additionally, residual or equilibrium concentrations can be predicted.

Types of Catalysts

Although many substances can be prepared to act as catalysts, only two types are prominent in the heterogeneous reactions prevalent in air pollution control. Noble metals, such as platinum, are the most efficient and commonly used metal catalysts. Transition metals, such as vanadium, are the second type.

Noble Metals

The noble metal catalysts (platinum, palladium, gold and silver)are usually deposited on an inert support to increase the exposed surface area. They are most efficient for catalyzing the oxidation reaction of hydrocarbons and maintain their reactivity to high temperatures.

These catalysts are susceptible to poisoning reactions with acid gases and erosion by particulates in the gas stream. Depositing them on metal carriers does, however, increase their resistance to abrasion.

Transition Metals

The most common transition metal catalysts include: vanadium, nickel, iron, cobalt, manganese and copper. Both the pure metals and thin oxides have catalytic properties which may be used in air pollution control systems.

Transition metal catalysts may be poisoned by absorption of inert gases, chemical reaction and erosion. Although they are easily poisoned, their lower cost and greater versatility are an advantage for air pollution control systems.

Methods and Parameters Used to Evaluate Catalysts

Catalysts vary in their reactivity and efficiencies for oxidizing the various air pollution emissions. Many of the parameters used to evaluate catalysts are dictated by the operating conditions of a particular process.

Optimum properties of a catalyst include: high deactivation temperature, resistance to poisoning, low initiation temperature and high efficiency. Although these criteria remain unchanged for all catalytic reactions, the means for obtaining the desired characteristics change with reaction type, reactants and reaction media.

Various catalysts have been studies by Anderson (1961), Stein (1960) and Dmuchovsky (1965) to define the "best" catalysts for effective oxidation of pollutants in terms of the above parameters. In general, the noble metals are the most efficient for hydrocarbon oxidations. The transition metals follow in the order: Co>Cr>Mn>Cu>Ni>V>Fe>Ti>Zn.

Catalytic activity is usually insensitive to the amount, chemical composition or the type of support used. The activity of metals deteriorates at elevated temperatures, and any catalyst selection must be made with thought of both efficiency and attrition at the operating temperature. After the selection of the catalyst, only the surface area and temperature are variable.

Unfortunately, the development of an optimum catalyst for a given set of conditions is not as yet relegated to the realm of scientific selection. Most of the synthetic work is proprietary with manufacturers and has not received much scientific correlation. In addition, the codification of catalysts is complicated by the combination of physical and chemical aspects which usually make the rate and products unique for each catalysts-reactant system.

6. Package Sorption Systems

Introduction

The study of sorbent types and sorption theories, as presented in Chapter 4, demonstrated that, of the several types of adsorbents available, activated carbons are better suited for gaseous air pollutant control than the others. Polar adsorbents such as silica gel, alumina gel and molecular sieves, adsorb water preferentially to the organic vapors while, conversely, activated carbons adsorb organic vapors preferentially to water vapor. Since moisture is invariably present in pollutant airstreams, only activated carbons can function effectively over any practical length of time. Activated carbons have an added advantage in that their adsorptive capacities are also larger for the organic vapors. The quest for adsorbent systems suitable for air pollution control thereby narrowed down to systems using only activated carbon. Polar adsorbents can be of limited interest in the adsorption of inorganic acid vapors or where the airstream is dry.

Activated carbon adsorbent systems, as presently manufactured for industrial and commercial uses, are oriented toward "air purification" and "solvent recovery". In the air purification application, the objective is to remove pollutants at trace level concentrations (1 ppm or less) to make the air suitable for breathing purposes. In the solvent recovery application, the adsorbent system is used to recover a solvent from a process exhaust stream. Profitable recovery is attained at concentrations above 500 to 1000 ppm, the lower level depending on the value and adsorptive properties of the solvent. The technology associated with these two applications is designated as "present technology" in this handbook and is discussed in considerable detail in this chapter.

Pollutants are, however, emitted into the atmosphere at concentrations ranging from less than 1 ppm to over 10,000 ppm. The concentration range from 1 to 500 ppm (the neglected range under present technology) is an important range in regard to pollutant emissions. Much of the "new technology" is concerned with development of control systems and procedures for this concentration range. These developments are also discussed in considerable detail in this chapter with emphasis on theoretical support for the various concepts proposed.

Both the air purification and solvent recovery systems are also suitable for applications where the primary objective is the purification of air exhausted to the atmosphere. Air purification systems would be effective where the pollutants are emitted at very low concentrations but need to be controlled because of their highly malodorous or toxic nature. These systems are cost effective only at low concentrations because of their nonregenerative design. At concentrations above a level somewhere in the range 1.0 to 10 ppm, the cost of more frequent carbon bed replacements would raise the air purification costs to levels above those of competing systems. Solvent recovery type systems in basic design are regenerative systems wherein the activated carbon bed can be regenerated within the system. At concentrations above 10 ppm, these systems purify air more economically than the nonregenerative type and their development, strictly for pollution control, forms the basis of the "new technology". Activated carbon regenerative systems whether for pollution control or solvent recovery are designated in this handbook as carbon resorb systems.

Basic Functions

Table 6-I presents the overall pattern of air purification and pollutant emission control in regard to pollutant concentration, odor level and emission sources. The types of pollutants encountered at the various levels that require control vary considerably and thereby the mode of control also varies.

In the concentration range below 1.0 ppm, the primary concern is with pollutants that are highly odorous or to some degree toxic or those that are oxidants as in smog. Pollutants of this type originate from combustion of fuels, incineration, and process industries such as meat rendering. Some industries emit reactants such as carbonyl chloride which are toxic at very low concentrations. Occupied spaces such as kitchens, bathrooms, offices, conference rooms, theaters and hospitals quickly develop malodorous atmospheres if not properly ventilated or the air purified by some means.

Solvents used by the solvent user industries do not contribute significantly to the low concentration odor problem except when the solvents are reactive to solar radiation and thereby contribute to smog formation. Except for 4-methyl-2-pentanone and xylene, solvents have odor recognition threshold concentrations that are over 5.0 ppm and TLV over 25 ppm; see Table 2-IV for odor and Table 2-III for TLV. Toluene and xylene, the solvents emitted in largest quantities, are highly reactive smog precursors, see Table 2-VIII.

Table 6-I Correlation of Pollutant Concentration with Odor Level, Emission Source, and Type of Adsorbent System Required

Pollutant conc., ppm	Qualitative odor level	Emission sources	Control device
0.05 to 0.1	Moderate odor	Seldom used space, non-airconditioned offices	Air-purification
0.5 to 1.0	Heavy odor	Highly polluted outdoor air, conference rooms	
5 to 10	Heavy odor	Emissions from process industries	Carbon-resorb systems
50 to 100	Moderate odor	Industrial plants	
500 to 1,000	Heavy odor	Solvent emissions from industrial operations	Solvent-recovery
5,000 to 10,000	Intolerable for continuous exposure	Solvent emissions from industrial operations	
50,000 to 100,000	Intolerable and deadly even for intermittant exposure	Safe only in closed cycle operations with inert atmosphere	

The basic function of control devices applicable in the low concentration range is to purify the indoor air and/or impure air brought in from outdoors so that it will be safe for breathing. The control devices used for this purpose are designated in this handbook as air purification systems.

When the would-be pollutant is a valuable solvent and is emitted in the 500 to 10,000 ppm concentration range, it is usually profitable to recover it for reuse with a solvent recovery system using steam for regeneration. Although the motivation is solvent cost savings, the solvent recovery system also functions as an air pollution control device. However, many solvent using operations utilize no control devices. In such cases the odor level can be very strong near the emission sources. On dilution with air mass movements, the concentrations become low enough to become nondetectable as odors. This point is reached with many solvents at 100 ppm and almost all solvents are nondetectable at 5 ppm.

A third concentration range extends from about 5 to 500 ppm. At the lower end of the range, the detectable and also offensive odors are those from meat and fish rendering plants, from incomplete incineration of refuse, from waste water treatment plants or any process where thermal or biological degradation takes place. At the upper end of the range, the pollutants are primarily solvents within the plant or neighboring areas to the plant. Pollutants in this (5 to 500 ppm) concentration can reach inhabited areas and cause damage to humans and property. Prevention of pollutant emissions here is a direct cost to the pollutor with the benefit of purer air going primarily to the neighboring inhabited areas; hence, their reluctance to spend funds for this purpose. This is the pollutant control area that requires considerable study to solve the many problems associated with it.

Air Purification Systems, Present Technology

General Discussion

Air purification is generally carried out in a partially closed system, i.e., the carbon-purified air is recirculated into the occupied spaces. When the air purification device is an integral part of the air conditioning system, make-up air from outdoors is added to the recirculating airstream in quantities ranging from 0% to 25% of the total volume. To maintain the CO_2 concentration below 1.0% - the upper acceptable concentration level - outdoor air (with CO_2 content of 0.03%) is required at make-up rate of 2 ft^3/min per person at rest and at 5 ft^3/min per person at work. This establishes the minimum make-up air input rate when the space per person ratio is relatively small. In large spaces where occupancy is small and intermittant, make-up air may not be required to maintain a low CO_2 concentration level.

A make-up air input rate of 5 ft^3/min per person is also sufficient to maintain the oxygen concentration above the 17% lower allowable limit.

If humidity and temperature are controlled by dryer and cooler outdoor air, the make-up air rate would be larger than the 5 ft^3/min per person as required for CO_2 control.

When the heating and/or cooling of the occupied spaces are a function of the ventilating system, the air recirculation rate would be determined by their requirements. The recirculation rate thus established also determines carbon bed area. For low pollutant emission rates the bed area thus determined may be larger than necessary.

Recommended fresh air or purified recirculated air requirements for general offices are 15 ft^3/min per person; for private offices, 25 ft^3/min per person; and for factories, 10 ft^3/min per person. The minimum requirement for factories is 0.10 ft^3/min per square foot of floor area or as governed by local codes (Perry Chemical Engineering Handbook, 1963). According to ASHRAE (ASHRAE Handbook of Fundamentals, 1967), the recommended fresh air or purified recirculated air to an occupied space with considerable air pollution as by tobacco smoke is 15 ft^3/min per person.

The above analysis establishes the recirculation rate at a minimum of 15 ft^3/min which includes at least 2 ft^3/min of outdoor air. Large auditoriums seating 2,000 people would then require an air purification device that can purify 30,000 ft^3/min of air. For a small room in a home, the other extreme in size, the required air handling capacity would be about 50 ft^3/min.

Figure 6-1 presents a flow diagram of a central ventilation system that incorporates the carbon bed and particulate filter elements as integral parts of the overall system. Not shown are the heating and/or cooling elements that are usually required. The ventilation systems may be one of earlier installation to which the particulate filter and carbon bed are attached. It is then necessary to find installation space for the air purification elements and also install a larger blower to overcome the added airflow resistance.

When no central ventilation system exists or it is not feasible to make the installation of the air purification elements, air purification for the occupied space can still be accomplished with a self-contained unit or true package sorbent device. These consist of a cabinet with influent and effluent airflow grilles, a blower, particulate filter and the carbon bed.

Small air purification devices consisting of one or two radial flow canisters and a blower are available for very small rooms.

Carbon Bed Designs

Common Characteristics - The carbon beds in air purification systems have very low L/D or L/A_c ratios. L/D is of the order of 0.01 where D is expressed as the diameter of a circular bed of area A_c. For comparison L/D for solvent recovery systems are of the order of 0.1. L is very short or more appropriately stated as being thin; depths of 0.5, 0.75, 1.0, 1.5, 2.0 and 3.0 in. are in frequent use. Bed areas are sized to control the airflow velocity in the 20 to 60 ft/min range with most units operated at about 40 ft/min. Coarse mesh carbons of 4 to 6, 4 to 8 and 4 to 10 fractions are used. The thin bed, the relatively low airflow velocity and coarse mesh all contribute to low airflow

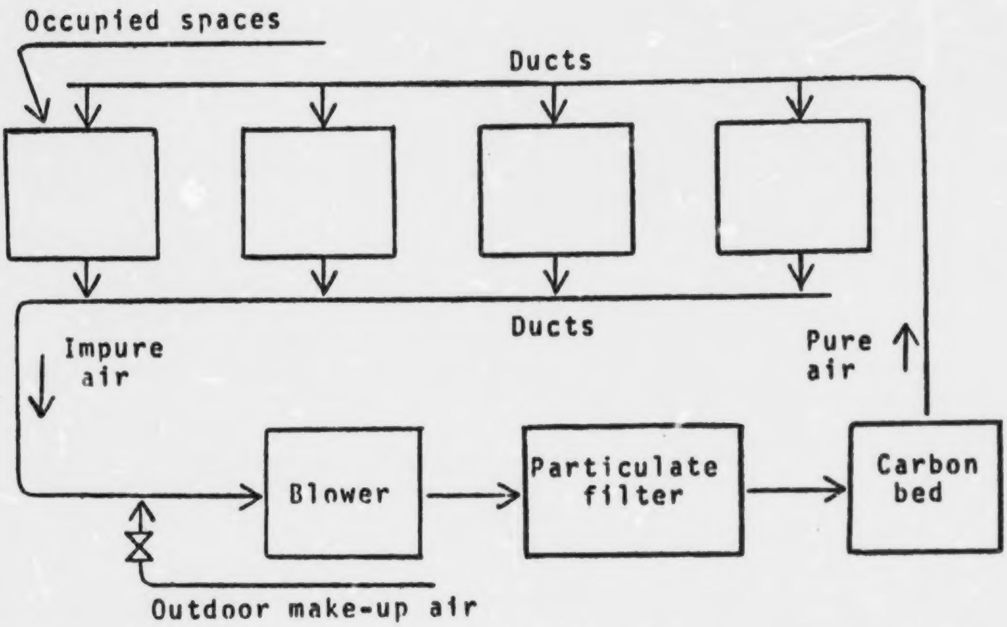


Figure 6-1 Central Ventilation System Showing Particulate Filter and Carbon Bed for Air Purification

resistances which are generally below 0.25 in. of H_2O pressure drop. An exception to the above are the air purification systems used in chemical-bacteriological-radiological (CBR) warfare service. Beds are thicker, usually 1.0 in. and over, and mesh size ranges are 6 to 8 and 12 to 30. Consequently the pressure drop is over 0.25 in. of H_2O. Safety against toxic agents is the overriding factor.

The thin, expanded-area carbon beds are attained by retaining the carbon between reinforced metallic screens or perforated sheets that are spaced apart to give the desired bed depth. The retainer can be shaped into various forms to provide advantages or economies in the assembly, operation and replacement of the carbon bed. The retainer can be in the form of a rectangular panel, also designated as a cartridge or tray. A number of the panels are inserted into a cell having a designed air-handling capacity of some definite flow volume such as 500, 1000 or 2000 ft^3/min. The retainer can also be one continuous piece folded back-and-forth or pleated across the depth of the cell.

The fold at each end can be rounded or v-shaped. Another approach, a carry-over from the gas mask, is the use of radial flow canisters. A number of canisters are attached to a manifold within the cell.

The cell is a unit of fixed or recommended capacity which can be combined with others to form a multiple cell unit of any desired total capacity. The multiple cell unit may be held together in a frame and inserted into the ventilating duct, thus appearing as an enlargement of the duct. In large installations, the multiple cell units are usually located in large walk-in cabinets or rooms. A very small air purifier may only consist of a small blower and one or two radial flow canisters.

Different manufacturers or fabricators specialize in one or more of the types of cell constructions described above. A list of carbon adsorbent systems manufacturers and/or vendors is given later in this chapter.

The following text briefly describes the various types of carbon beds commercially available.

Panel and Pleated Carbon Beds - Figure 6-2 illustrates a nine-cell carbon filter, a cross-sectional side view of a cell and two carbon panels. The dimensions of the panels produced by different fabricators vary some, but are generally in the ranges 2 by 2 ft, 2 ft by 8 in and 1 ft by 8 in. The cell front is usually 2 by 2 ft and depth varied from about 2 ft to 8 in. The number of panels per cell can vary from 10 to 24. Carbon loading for a cell varies between 45 to over 95 lb per 1000 ft^3/min airflow rate. Ease of removal and replacement of the carbon bed is an important consideration in regard to operating costs. With this type cell the carbon panels can be readily pulled out and replaced by simply removing the front grille which holds the panels in place. Seals are not a critical problem except for the CBR filters. In some carbon filters, such as used in some toxic agent air purification systems, the panels are parallel rather than slanted toward each other.

Figure 6-3 shows one type of CBR filter for a small protective shelter. The carbon bed area is one square foot, hence at the 48 ft^3/min flow the air velocity is 48 ft/min. This filter meets the shelter requirements of up to 12 people, which gives a minimum purified air change of 4 ft^3/min per person.

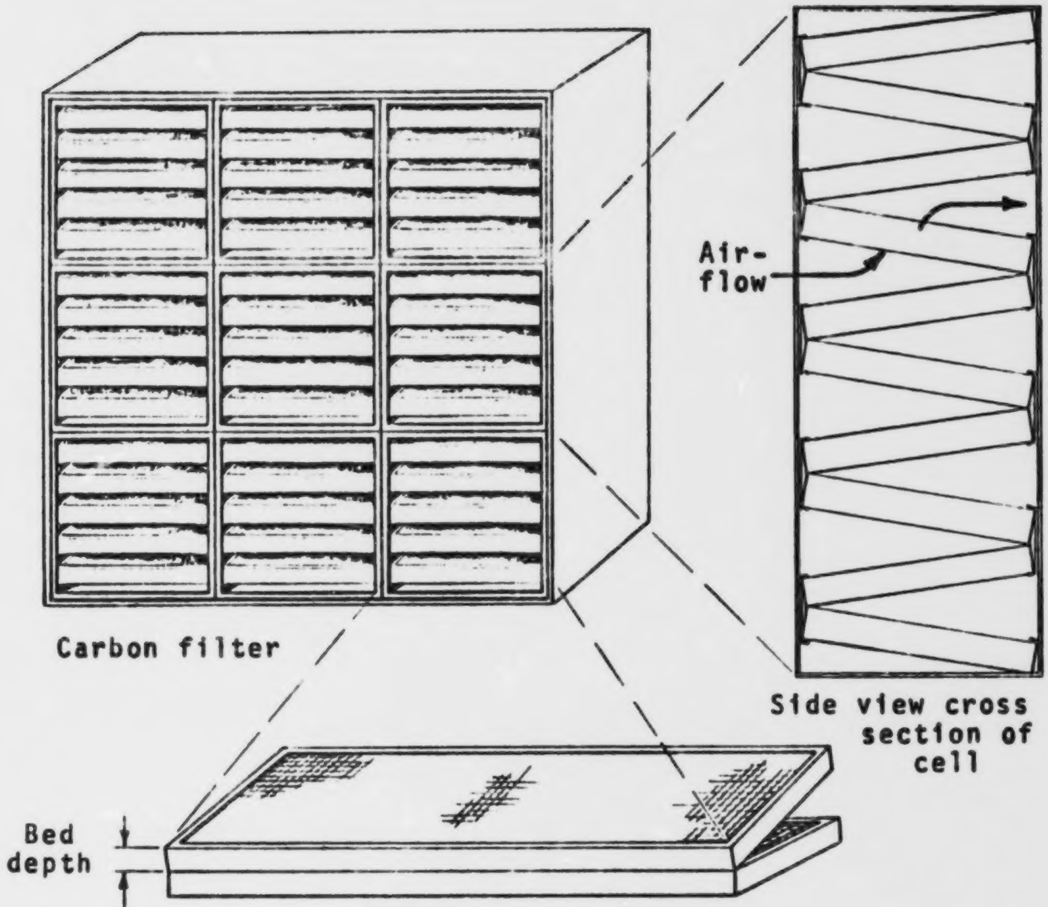


Figure 6-2 Multiple Cell Activated Carbon Filter for Air Purification

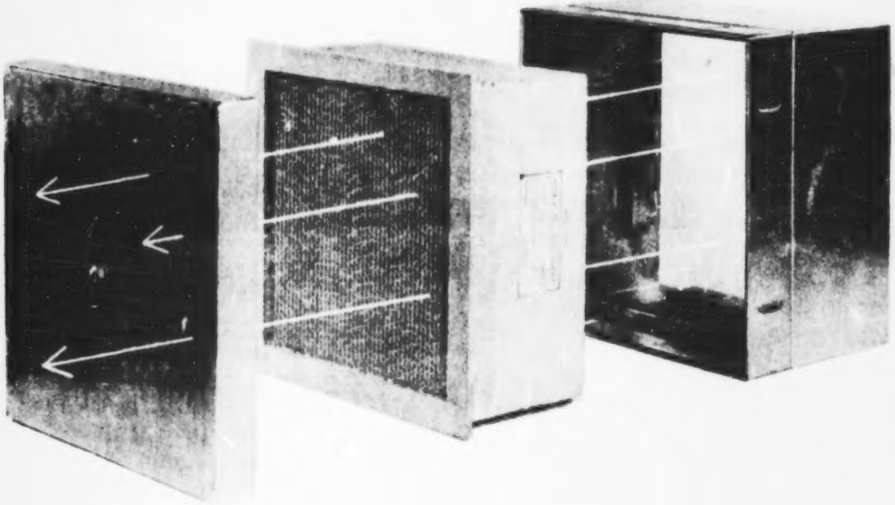


Figure 6-3 A Chemical-Biological-Radiological Filter, Size 12 by 12 by 8 in., Operated at 48 ft^3/min for Small Protective Shelters. Courtesy MSA Co.

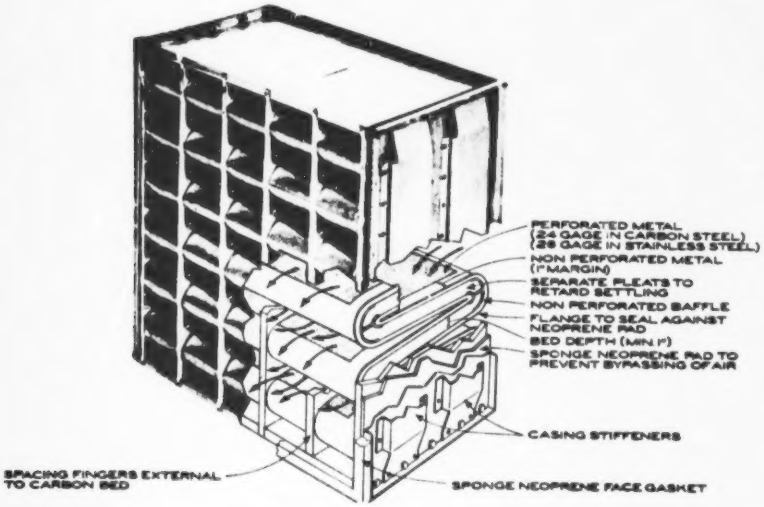


Figure 6-4 Pleated Type Carbon Filter for Control of Radioactive Pollutants, Size 24 by 24 by 11.5 in., Operated at 1000 ft^3/min Flow. Courtesy of MSA Co.

Dimensionally the pleated carbon beds are not greatly different from the panel type. Figure 6-4 shows the general exterior appearance and a cutaway section shows the internal construction. This carbon filter or cell is of particularly rugged design for use in nuclear reactor facilities to control radioactive pollutants that might be released accidently. Its operating capacity is 1,000 ft^3/min at 1.0 in. of water pressure drop and pollutant removal efficiency greater than 99.99%. The cell size is 24 by 24 in. front dimensions and 11.5 in. deep. With 12 horizontal sections the carbon bed area is approximately 20 ft^2 and air flow velocity 50 ft/min. Bed depth L is 1.0 in. or deeper. For non-CBR use, pleated bed cells are simpler in construction, L is usually less than 1.0 in., and coarser carbon is used.

The pleats may be horizontal as in Figure 6-4 or vertical. To unload the spent carbon, the cell is removed from the multiple cell filter and one of the plates at the end of the pleats removed.

Canister Carbon Beds - Figures 6-5, -6 and -7 show: (1) the construction of one type of canister, (2) their assembly into the cell and (3) a small self-contained air purifier. Specifications are given for two canisters, a Type 28 with 0.5 in. bed thickness and a Type 42 with 0.75 in. bed thickness. The mean area, between outer and inner retainer screens, for Type 28 is approximately 0.73 ft^2 and for Type 42, approximately 0.76 ft^2. The recommended maximum capacity for Type 28 canister is 30 ft^3/min. At this flow the pressure drop is 0.15 in. of H_2O and flow velocity approximately 41 ft/min. For Type 42 canister the recommended maximum capacity is 25 ft^3/min which gives a 0.16 in. of H_2O pressure drop and 33 ft/min flow velocity. For a filter or cell of 1,000 ft^3/min flow capacity, 33 canisters of Type 28 are needed and 40 of Type 42.

Figure 6-6 shows a filter where the manifold plate is in a slanted position. Vertical and horizontal plate positions are also used. In this filter construction, the canister is held to the plate by means of a bolt passed through the center. By loosening a wing nut, the spent canister can be easily removed for replacement with a fresh canister. The flow direction is from the outside to the center of the canister. This flow direction is preferred to a flow in the reverse direction because it gives a shorter adsorption zone length.

Materials of Construction

The carbon-cartridge frames, cell frames and other enclosing panels and supporting structures are mild steel when pollutant vapors are noncorrosive. Under operations

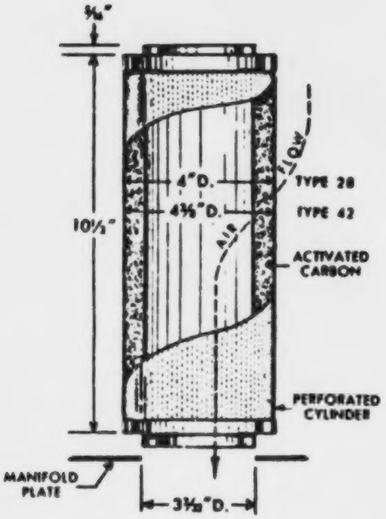


Figure 6-5 Radial Flow Canister Design for Air Purification Systems. Courtesy of Connor Engineering Corp.

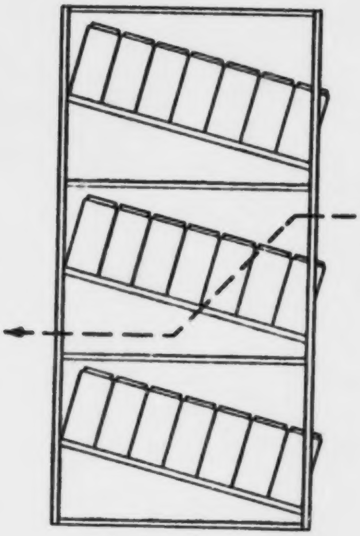


Figure 6-6 Arrangement of Canisters on a Slanted Manifold Plate for Medium and Large Air Purification Systems

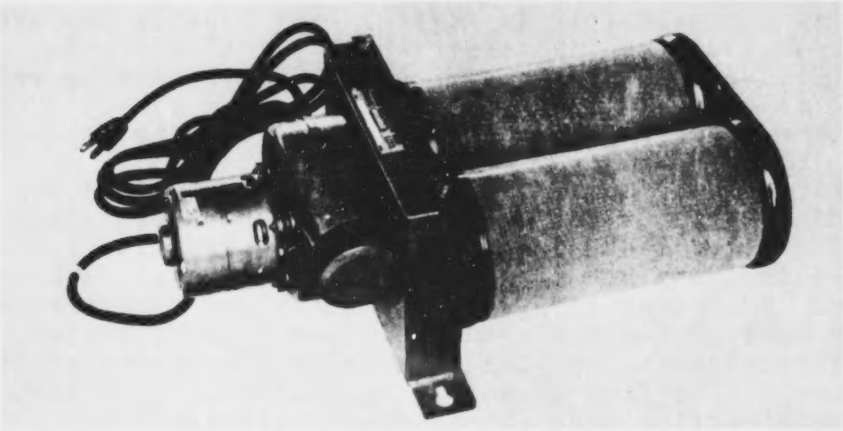


Figure 6-7 Self-Contained Canister Type Air Purifier for Small Occupied Spaces. Courtesy of Connor Engineering Corp.

where considerable moisture can enter the cells or corrosive vapors are present, special coatings are applied to the steel. Zinc-plated and chromate finishes are mentioned by some manufacturers. Some attention is also given to prevention of air leakage around the cartridges. This can be done by interlocking construction, felt seals, or caulking. The place where corrosion is most likely to occur is at the interface between the carbon and retainer screen. Moist carbon or carbon containing corrosive pollutants establish galvanic cells at the interface and corrosion proceeds rapidly. Stainless steel or plastic retainer screens are required under conditions where this can happen.

Operation of Air Purification Systems

Operating Parameters - To attain the most effective and economical service from air purification systems, various parameters need to be optimized. These parameters are flow velocity, carbon mesh size, and bed thickness. They determine the resistance to flow, the adsorptive capacity (assuming selection of carbon has already been made) and carbon bed area. Another important factor is the determination of the optimum service time at which the carbon bed should be replaced. Temperature is not a controlling factor in air-purification as it very often is in other pollutant control applications. Occupied spaces are generally in the 50° to 90°F temperature range, a range in which activated carbons perform effectively. Pollutant concentration is also an important factor that should be recognized because of its effect on capacity and service time.

Flow Velocity - An increase in flow velocity produces an increase in pressure drop through the bed and an increase in adsorption zone length. Both increases are undesirable. An increase in pressure drop raises the power requirements to operate the blower, and an increase in adsorption zone length decreases the overall adsorptive capacity. Conversely a decrease in flow velocity produces a favorable effect in these two properties of the system, but the decrease in flow velocity is accomplished by increasing the bed area. The added panels, pleated cells or canisters represents an increase in investment. When the pollutant is not extremely toxic, a balance in cost factors has been worked out so that most systems have bed thicknesses of 0.5, 0.75 and 1.0 in. and are operated at about 40 ft/min flow velocity. A coarse mesh size falling in the range 4 to 10 mesh is used, giving pressure drops that are below 0.25 in. of water. Some sacrifice is made on complete purification; the efficiency specification is about 98%.

Filters for toxic agents contain larger mesh carbons, 12 to 30, and are thicker, 1.0 in. and over. Efficiencies over 99.99% are required. The pressure drop is higher because of the smaller carbon granules and thicker bed.

Pressure Drop - The pressure drop through the carbon bed is a function of the carbon granule size, the size distribution, the packing of the bed and flow velocity. Equation 4-43 shows the relationship between the pressure drop and flow velocity, mean particle diameter and void volume, ε, between the granules. ε is dependent on the mesh size distribution and degree of packing of the bed. ε can be calculated if the particle density of the carbon and bulk density of the bed are known, but usually ε is the unknown variable.

Figure 6-8 presents several curves that show the effect of mesh size fraction and flow velocity on the pressure drop. These curves were recalculated from curves given in Union Carbide Corp. Catalog Section 3-6450, Data Sheet No. 1.

Service Time - The service time of the filter is a function of the flow velocity, influent pollutant concentration and the adsorptive capacity of the selected carbon for the particular pollutant under consideration. Equations 4-23 and -24 establish the relationships between these variables for flow systems in which the bed is equal to or deeper than the adsorption zone length at steady state. Because of the coarse carbon granule size and thin beds that are used in air purification systems, the bed depth is usually considerably shorter than the adsorption zone. Equation 4-24 does not then apply, except to indicate an upper limit on service time.

From Figure 4-17, L_Z at $U = 40$ ft/min is 1.7 in. for low molar-volume odor molecules in coarse 4 to 10 mesh carbon beds. L_Z increases to 2.3 in. for high molar-volume odor molecules. When carbon beds of 0.5, 0.75 and 1.0 in. thickness are used, pollutant penetration of the bed occurs long before the adsorption zone has attained steady state. The adsorption zone is in a transitory state during the whole service time as depicted by Curves 1 and 2 in Figure 4-13. Pollutant penetration of the bed occurs early in the service time but because of the low influent concentration the effluent concentration rises very gradually with time. High 99.99% pollutant removal efficiencies are not attainable, but at 98% efficiency, practical service times are attainable.

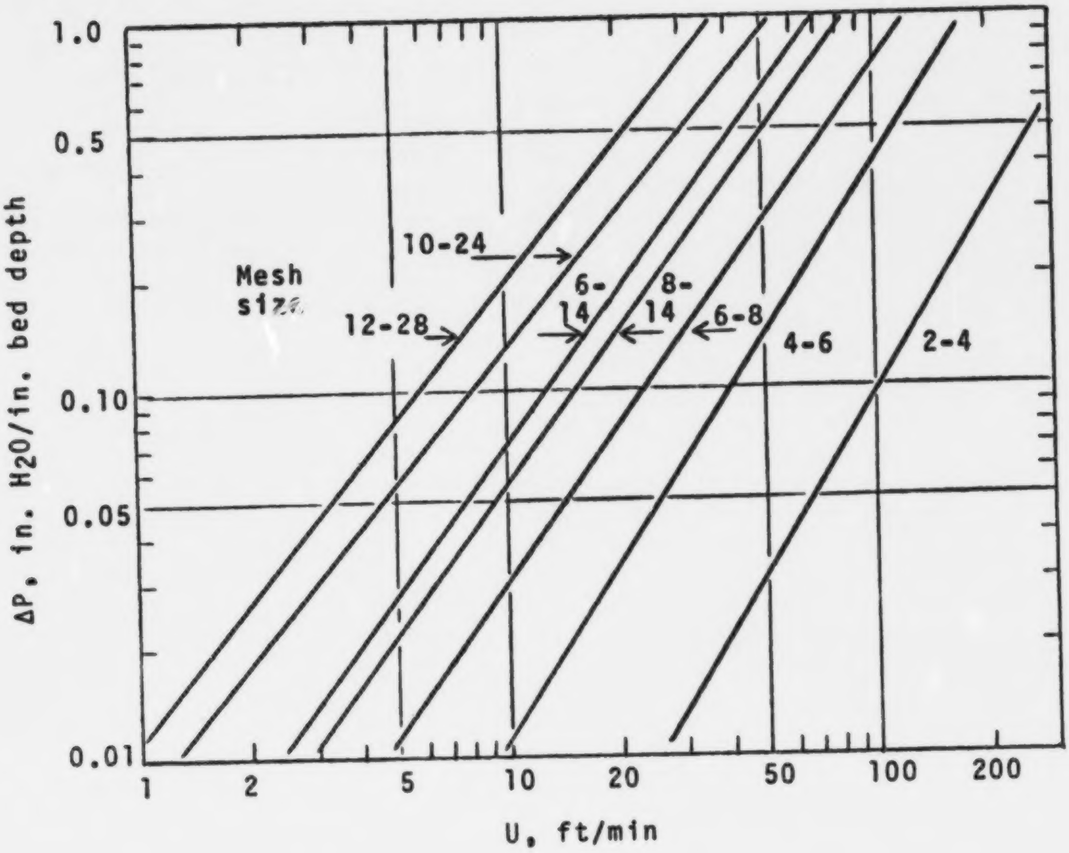


Figure 6-8 Pressure Drop Through Granular Carbon Beds of Varied Mesh Size Fractions as Function of Flow Velocity

When a finer 12 to 30 mesh carbon is used, L_z range is from 0.6 to 0.8 in (at $C_b/C_i = 0.01$). In carbon beds of 1.0 in. and over, the L_z has attained steady state and is contained within the bed depth. This state is depicted by Curve 3 in Figure 4-13. Pollutant removal efficiencies of 99.99% and over are attainable because the adsorption zones of length greater than 0.6 to 0.8 can be contained in the bed, i.e., zones measured to $C_b/C_i < 0.01$. See Chapter 4, Dynamic Adsorption Process for further discussion.

The service times attained vary from 6 mo, when the odor concentration is described as heavy, to much longer periods of up to 2 yr, when odor concentration is light. Odor concentrations are not often quantitatively defined in terms of ppm since odors are not always identified with specific compounds and a direct quantitative measure made. Operating efficiencies of 98% (i.e., $C_b/C_i = 0.02$) are considered acceptable and when the efficiency has decreased to about 90% (i.e., $C_b/C_i = 0.10$), the carbon bed is replaced.

Equation 4-24 was used to estimate t_b at $L = L_z$, $U = 40$ ft/min and $C_i = 0.5$, 0.1 and 0.05 ppm for 4 to 10 mesh carbon. 4-Methyl-2-pentanone was used to represent the odor and BPLV the vapor phase activated carbon. For this system and conditions, $L_z = 2.1$ in. when $C_b/C_i = 0.01$. Since the bed depth in common use are considerably less than L_z, the true t_b for $L<L_z$ are then progressively smaller as L is smaller than L_z. The procedures for carrying out the calculations are described in Chapter 4, Determination of Service Time. The results are as follows:

C_i	t_b, da
0.5	15
0.1	53
0.05	92

These t_b are continuous service times and are low compared to actually attained service times of 180 to 730 da, although based on a much deeper bed depth. This is an indication that the prevailing concentrations may be considerably lower than given above and, also, that the system is exposed to highly intermittent exposure to odor vapors.

Odor Concentration - Some of the more probable odors that air purification systems are required to control are the first 23 pollutants listed in Table 2-IV. To this list may be added smog-created vapors, odor vapors generated in washrooms and two additional odor vapors emitted from rendering plants. The odor vapors are:

Pollutant	Source
Skatole, 3-methyl-1-benzo(b)pyrrole	Washroom
Indole, 1-benzo(b)pyrrole	Washroom
Putrecine, 1,4-diaminobutane	Washroom
Cadaverine, 1,5-diaminopentane	Washroom
Propanoic acid	Rendering
2-Methyl propenal	Rendering

The recognition threshold concentrations of the above 23 designated pollutants range from the lowest, 0.0002 ppm, for trimethylamine to the highest, 1.0 ppm, for nitrogen dioxide. The recognition threshold concentration for skatole has been reported at 7.5×10^{-8} ppm and 0.019 ppm by two different investigators. Threshold concentrations were not found for the others listed above, but they are expected to be low although higher than 0.0002 ppm.

The odor recognition threshold places an upper limit to the odor-vapor concentration level that the air purification system can deodorize. With intermittent release of odor vapors and recirculation of the air, the air purification system need not remove the odor vapor concentration all the way down to the recognition threshold on a single pass. The repeated passage through the carbon bed will bring the odor concentration down gradually to and below the recognition threshold. Also, odor vapors are not equally obnoxious so that some may be tolerated considerably above the threshold concentration.

An air purification system operating at 98% efficiency can deodorize air containing trimethylamine in a single pass if the concentration does not exceed 0.01 ppm. With recirculation the initial concentration level can be higher but the odor will be detected for a longer time. For skatole the initial odor vapor concentration can be at about 1.0 ppm. For nitric oxide the initial concentration can be 50 ppm, but at this concentration, and down to at least 10 ppm, the carbon resorb system would be more economical to operate. Odor vapor concentrations in the range 1.0 ppm and down are realistic for the airflows to be deodorized with the above described air purification systems.

Carbon Bed Replacement - To attain the maximum but uninterrupted service from a carbon filter, it would be desirable to monitor the progress of the adsorbed-phase profile through the carbon bed so that the service time could be determined at which the carbon filter should be replaced. The other-wise generally low capital cost of the cell (about \$60 to \$80 per 1000 ft^3/min capacity at manufacturing cost) does not warrant high expenditures for monitoring instruments that can determine this service time precisely. However, a determination can be made of the service time by means of a test element attached to the influent face of one of the cells. From prior experience with the same purification system or with other similar systems and operating conditions, an approximate service time is already known. Prior to the estimated service time, the test element is removed from the cell and sent to the system's manufacturer for analysis and determination of the remaining service time.

The spent panels, cells or canisters are shipped to the system's manufacturer where they are emptied and reloaded with reactivated or virgin carbon. Special procedures are used in the reloading process to insure tight packing of the carbon and thereby avoid later settling of the carbon during transit or usage. Poorly packed beds can develop open areas through which the impure air can pass. The carbon is returned to its manufacturer where it is reactivated with high temperature steam to its original capacity. Some handling and activation losses occur on each cycle, which can be as high as 5%. Over a number of cycles, the used carbon is completely replaced with virgin make-up carbon. The air purification systems user gets credit for the returned spent carbon; the cell replacements are less costly than the initial purchase.

Solvent Recovery Systems, Present Technology

General Discussion

The solvent recovery systems have been developed to a high degree of efficiency and reliability. The technology on solvent recovery is also well documented in literature. The purpose of this part of the chapter is to summarize this technology and in the next part of the chapter to explore ways whereby this technology can be expanded to applications that are unprofitable but concerned strictly with decreasing pollutant emissions.

Process engineers and equipment designers have directed their efforts to improve the economics of solvent recovery operations. These efforts have been directed toward decrease of power or fuel requirements for regeneration, reduction of pressure drop during the adsorption phase, increase of adsorptive capacity by utilizing residual capacity of adsorption zone, and improved methods for recovery of the desorbed solvent. The result has been the development of three types of systems differentiated by the manner in which the carbon bed is maintained or handled during both phases of the adsorption-regeneration cycle. These are:

Fixed or stationary bed
Moving bed
Fluidized bed

The selection of the system depends on the type of solvent vapor and the circumstances under which it is to be recovered.

The most efficient and economical service is obtained from the solvent recovery system, regardless of type, if the airflow is kept at a minimum but in keeping with proper ventilation. In a plant with well defined operating units that emit pollutant vapors, the airflow can be kept low by use of closely fitting hoods over the operating units and the hoods connected by way of ducts to the pollutant control system. By use of close fitting hoods, sufficient draft is created to draw the pollutant away from the point of emission with use of minimum airflow. Such situations can be taken advantage of in degreasing (Figure 1-1), dry cleaning (Figure 1-2), rotogravure and flexographic presses, the various surface coatings applications, rubber products dipping operations, paper impregnating operations and surface coating and ink drying ovens. When a new plant is being contemplated, the pollutant control system should be considered as an integral part of the plant. This would involve an effort on the part of the machinery designers and plant layout men.

Figure 6-9 presents a flow diagram of a dual, stationary bed, solvent recovery system with auxiliaries for collecting the vapor-air mixture and for solvent separation from steam condensate. The vapor-air mixture, collected from the various point sources, passes through the particulate filter and into the on-stream carbon adsorber, in this case the upper one. The effluent air, which is virtually free of vapors, is usually vented outdoors. In this diagram the blower precedes the particulate filter; in many applications the blower follows the particulate filter. The lower carbon adsorber is regenerated during the service time of the upper adsorber. A steam generator or other source of

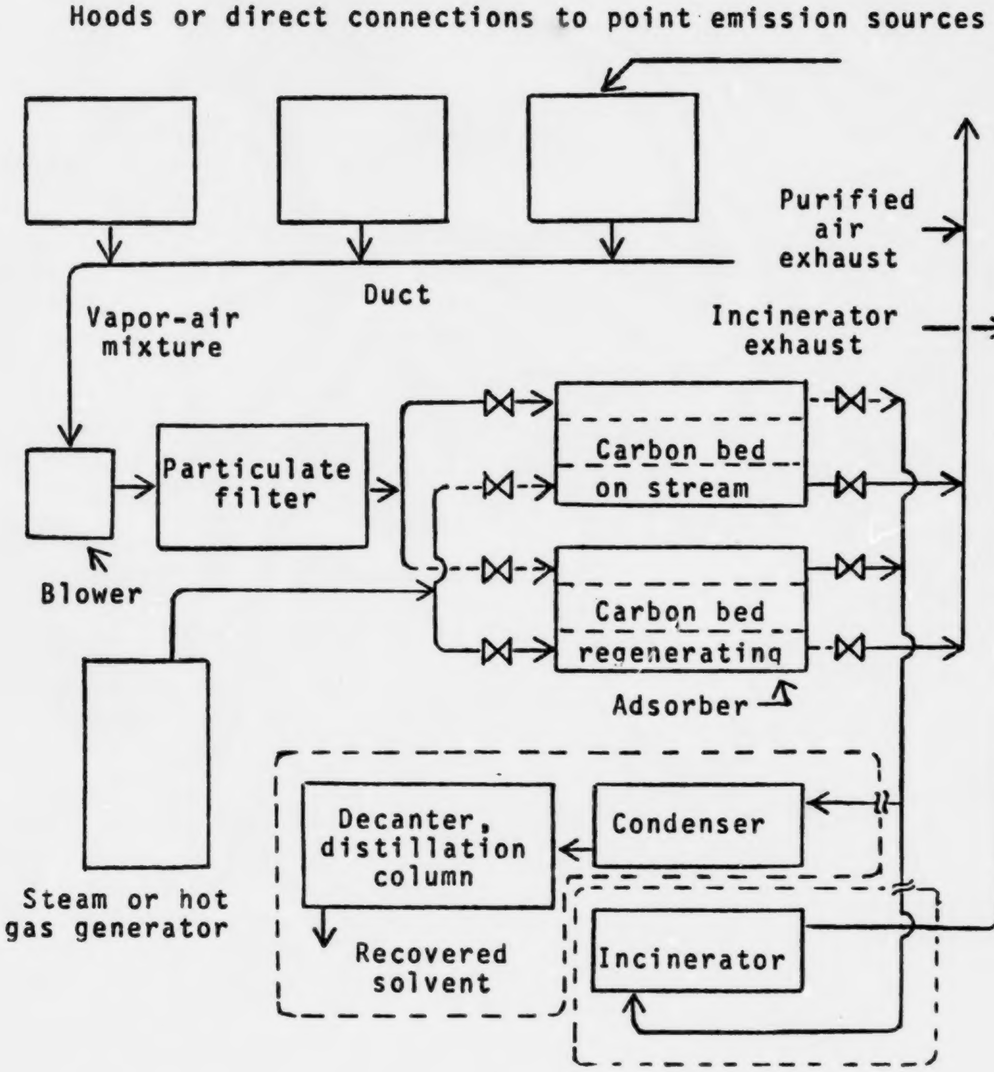


Figure 6-9 Stationary Bed Carbon Resorb System with Auxiliaries for Vapor Collection and Solvent Separation from Steam Condensate or Incineration of Pollutant Vapors

steam is required. The effluent steam-solvent mixture from the adsorber is directed through the condenser and the liquified mixture then run into the decanter and/or distillation column for separation of the solvent from the water.

Other carbon resorb systems can be used in place of the dual, stationary bed system as the circumstances warrant.

Stationary Bed Systems

Figures 6-10 to -13 show two designs of stationary bed, solvent recovery systems. The type shown in Figures 6-10 and -11 employs vertical cylindrical beds wherein the solvent-laden air flows axially down through the bed. This particular design is advertised for use in recovery of solvents used in degreasing and dry cleaning although equally well suited for recovery of solvents from other industries. Solvents mentioned are trichloroethene, tetrachloroethene, toluene, Freon TF and dichloromethane. Regeneration is with steam up-flow through the bed and, since the above mentioned solvents are immiscible in water, decantation is used to separate the condensed solvent from the steam condensate. The valves are disk type, open and close by pistons. Water is used as coolant in the condenser. Steam, electric power to drive the blower, and cooling water are three operating cost items. Cost of steam and cooling water increase with frequency of regeneration.

Figure 6-11 shows the external features and arrangement of the component parts of a two-adsorber system. This particular unit is a Vic Model 572 AD, with two adsorbers used alternately, i.e., while one adsorber is on-stream the other is regenerating. The recommended airflow capacity is 3,000 ft^3/min for each adsorber of approximately 5 ft diameter and bed length near 20 in. This adsorber model was used as a basis for the calculation of bed depths and adsorbed-phase profiles, Chapter 4, page 59, and regeneration of activated carbons, Chapter 4, page 67.

Dual adsorber systems are also operated with both adsorbers on stream in parallel when the solvent concentration is low. Regeneration is less frequent than every hour and may be done during off-working hours. Operation in parallel almost doubles the air handling capacity. The capacity of Model 572 AD increases to 5,500 ft^3/min.

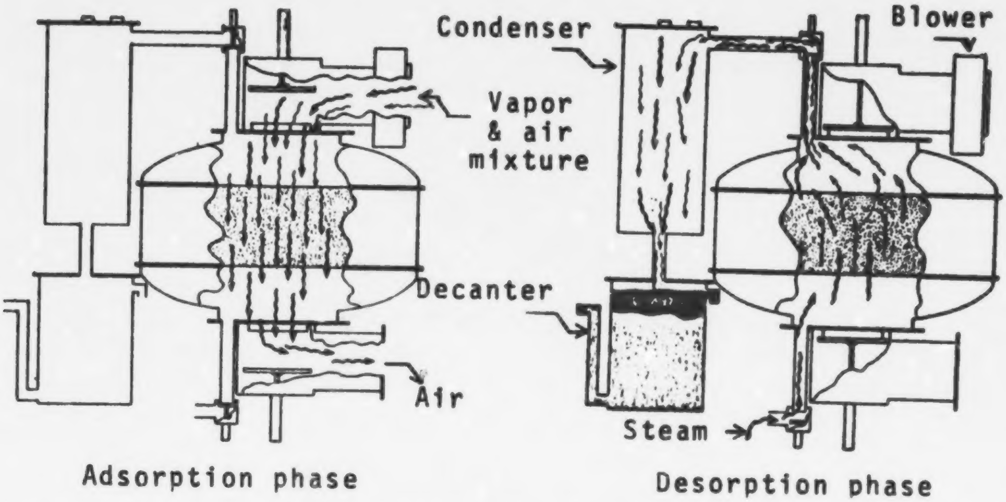


Figure 6-10 Cut-Away Diagram of Solvent Recovery Adsorber, Showing Vapor-Air Flow Pattern During the Adsorption and Steam Flow During Desorption. Courtesy of Vic Manufacturing Company.

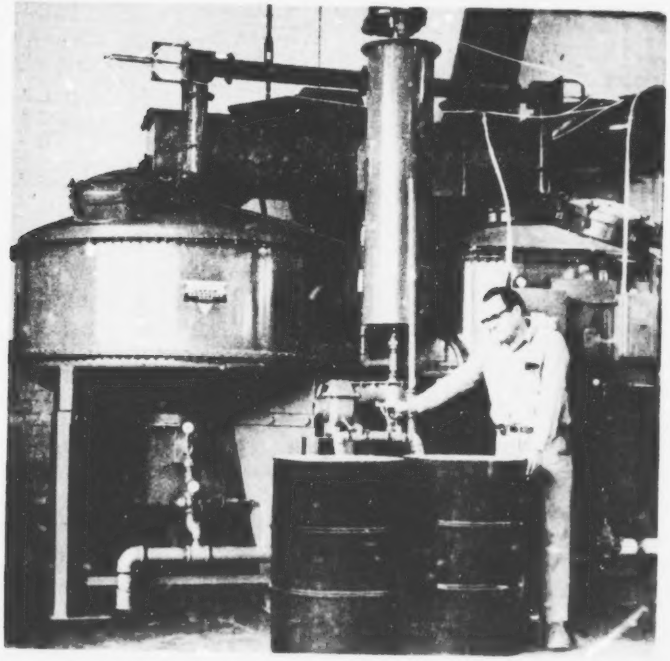


Figure 6-11 Stationary Bed Solvent Recovery System of 3000 ft^3/min Flow Capacity for Each Adsorber. Used for Water Immiscible Solvents. Courtesy of Vic Manufacturing Company.

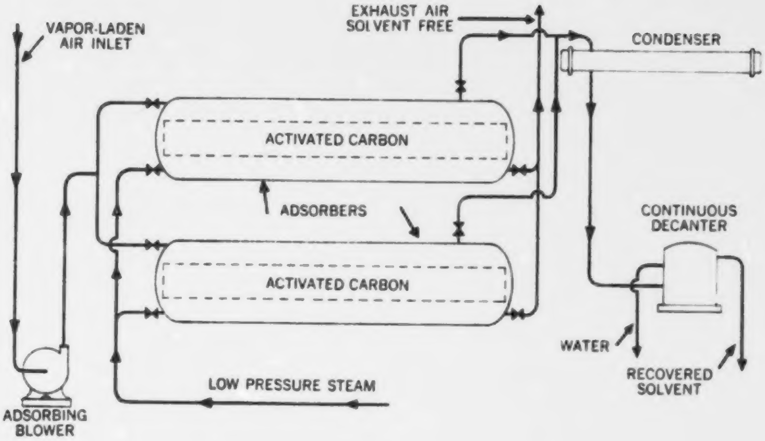


Figure 6-12 Flow Diagram of a Solvent Recovery System Courtesy of Vulcan-Cincinnati, Inc.

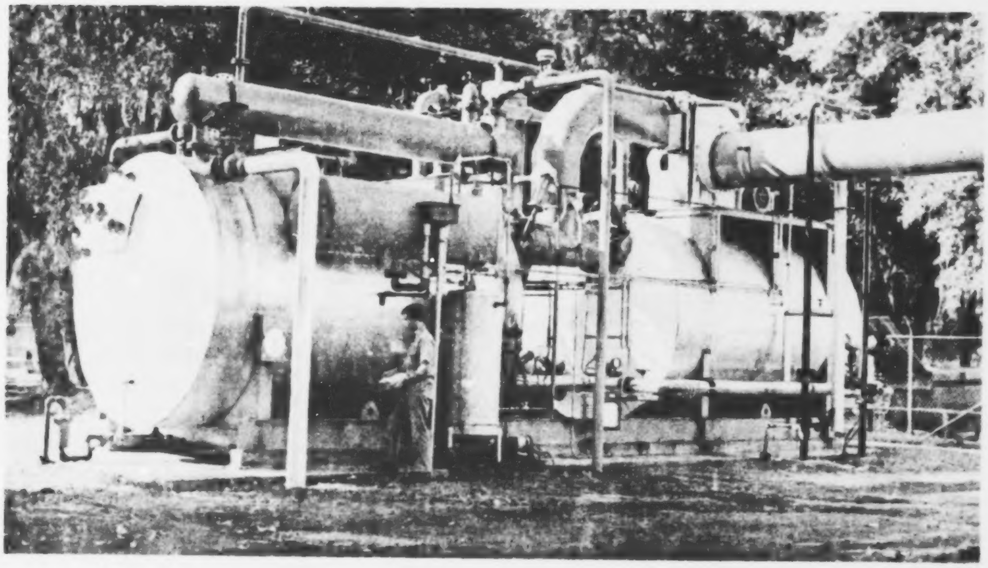


Figure 6-13 Solvent Recovery System for Recovery of Naphtha from a Rubber Products Plant, 12,000 ft³/min Flow Capacity. Courtesy of Vulcan-Cincinnati, Inc.

For a one-hour adsorption-regeneration cycle time, the sales literature reported recovery of trichloroethene is 225 lb and steam requirement for regeneration is 675 lb, giving a steam-to-solvent ratio of 3.0. This is typical for a high solvent concentration level. The solvent recovery and steam requirements as given in Table 4-XVIII for Profile 3 are 180 lb/hr of solvent, 500 lb/hr of steam giving a steam-to-solvent-ratio of 2.8 at solvent concentration of 3,000 ppm. The good agreement between the steam-to-solvent ratios is an indication of the reliability of the methods used to calculate the theoretical 2.8 ratio.

The largest vertical or up-right adsorber constructed by Vic Manufacturing Company has an airflow capacity of 5,000 ft^3/min with carbon bed diameter of about 6 ft. The overall length and width dimensions are 18 and 11 ft and overall height 11 ft. The smallest has a 700 ft^3/min airflow capacity and overall dimensions 7 by 5 ft, length and width, and 11 ft height. All of these units fit into the general concept of packaged sorption devices.

The horizontal tank type adsorber as illustrated in Figures 6-12 and -13 are structurally more amenable to large capacity solvent recovery systems than the vertical type, although Vulcan-Cincinnati, Inc. engineers systems as small as 2,000 ft^3/min. The 2,000-ft^3/min system, designated as Model 22, has two adsorbers, overall length and width dimensions are 18 and 7 ft and overall height is 13 ft. The largest system, designated as Model 403, has 40,000 ft^3/min air flow capacity, overall length and width dimensions are 52 and 27 ft and overall height is 26 ft. Their largest skid mounted system, Model 102, has design capacity of 10,000 ft^3/min, overall length and width dimensions are 38 and 12 ft and overall height is 16 ft. Units of size Model 102 are basically off-the-shelf packaged sorbent devices while units of size Model 403, fall into the broader definition of a packaged unit in that they can be transported and later assembled from smaller components.

This type of solvent recovery system is successfully being used in a variety of industries. To follow the industry category system presented in Table 1-II, the industries in which they are in use are, plastics, rubber products, adhesives and paper coatings. Two other industries not included in Table 1-II, although mentioned on page 1-67, are pharmaceuticals and chemical manufacturing. Solvents that are being recovered are listed below with their V_m.

molar volumes, to indicate their relative adsorbabilities:

Solvent	V_m, cm³ liq/mol	Solvent	V_m, cm³ liq/mol
Heptane	163	Ethyl acetate	106
Naphtha, 240°-340°F	140-207	Butanone	96
Xylene	140	Benzene	95
4-Methyl-2-pentanone	140	Tetrahydrofuran	88
Hexane	140	2-Propanol	84
Freon TF(1)	120	Propanone	74
Cyclohexane	118	Dichloromethane	65
Toluene	118	Ethanol	61
2-Ethoxy ethanol	116	Ethanenitrile	51
Diethyl ether	106	Methanol	42

(1) 1,1,2-Trichloro-1,2,2-trifluoroethane

These solvents are frequently used also in surface coatings and graphic arts industries, particularly toluene, xylene and 4-methyl-2-pentanone. The solvent recovery systems would also be effective in these two industries although not specifically identified among the systems' users. Table C-I identifies these and other solvents with various pollutant emission sources.

The flow diagram of Figure 6-12 shows one horizontal carbon bed in each adsorber. This type of adsorber is also fabricated with two beds, one above the other. The airflow enters the adsorber between the beds with up-flow through the upper bed and down-flow through the lower. This reduces the adsorber shell size for a given flow, thereby reducing construction costs.

The solvent recovery system illustrated in Figure 6-13 is the Vulcan-Cincinnati, Inc. Model 102 designed to operate at 10,000 ft³/min airflow. In this particular application, it is operated above design capacity, 12,000 ft³/min, to recover naphtha from a rubber products plant. The bed area in each adsorber is about 110 ft² and bed length is 16 in. At the 12,000 ft³/min flow, the linear velocity through the bed is approximately 110 ft/min. It is operated on a one hour adsorption-regeneration cycle, recovering on the average 293 lb of naphtha per cycle. Steam consumption is about 1770 lb per cycle which, on an average, gives a 6 lb steam/lb naphtha ratio. The carbon bed volume is approximately

145 ft^3 and, when loaded with carbon of 31 lb/ft^3 density the bed weight is 4,500 lb. For the 293 lb/cycle recovery the operating capacity is then 0.065, with no correction being made for the adsorption zone.

The naphtha being recovered is an aliphatic-naphthenic petroleum fraction boiling in the 240° to 340°F range. Normal and branched chain aliphatic hydrocarbons, cyclooctane, and substituted cyclohexanes and cycloheptanes of C_7 to C_{10} fall into this boiling range. Most of these solvents are included in Table C-I. Their odor recognition threshold and TLV concentrations are relatively high and they are not particularly reactive to solar radiation. They can pass into the atmosphere unnoticed at low concentrations.

The theoretical steam-to-naphtha ratio for the above recovery operation is 7.2 (compared to the measured 6.0) when cyclooctane is used to represent naphtha in the calculations.

Figure 6-14 illustrates a small, cabinet-enclosed, single adsorber, solvent recovery unit. Hoyt Manufacturing Corp. advertises four models; the one shown is Model 4. It is designed for use in plants using up to 3 drums (165 gal) of solvent per month at airflow capacity of 700 ft^3/min. Its overall dimensions are 49 by 45 in., length and width, and 81 in. height. These units are piped directly to the production machine emitting the solvent (or pollutant). In an existing plant where the use of vapor collection ducts to a central solvent recovery system are not feasible, the use of a number of small directly connected units may be the solution to an otherwise difficult problem.

Figure 1-2 presents a flow diagram of a solvent recovery system as an integral part of a coin-operated, dry cleaning machine. The solvent used is Freon TF, 1,2,2-trichloro-1,2,2-trifluoroethane, which has a $V_m = 120$ $cm^3 liq/mol$ and 118°F boiling point. It is relatively volatile yet strongly adsorbed. It is not a strong pollutant in regard to odor, toxicity or as a smog precursor.

Two sizes of dry cleaning machines of the above type are manufactured. The smaller size machine cleans an 8-lb load of clothing and the larger commercial size a 25-lb load. One gallon, or 13.3 lb, of Freon TF is required per pound of clothing in the washing and rinsing phases of the cleaning cycle. After the rinsing phase the Freon TF is drained from the washer-extractor and clothing tumbled while air at about 85°F is passed through the tumbler. The vapor-laden air-

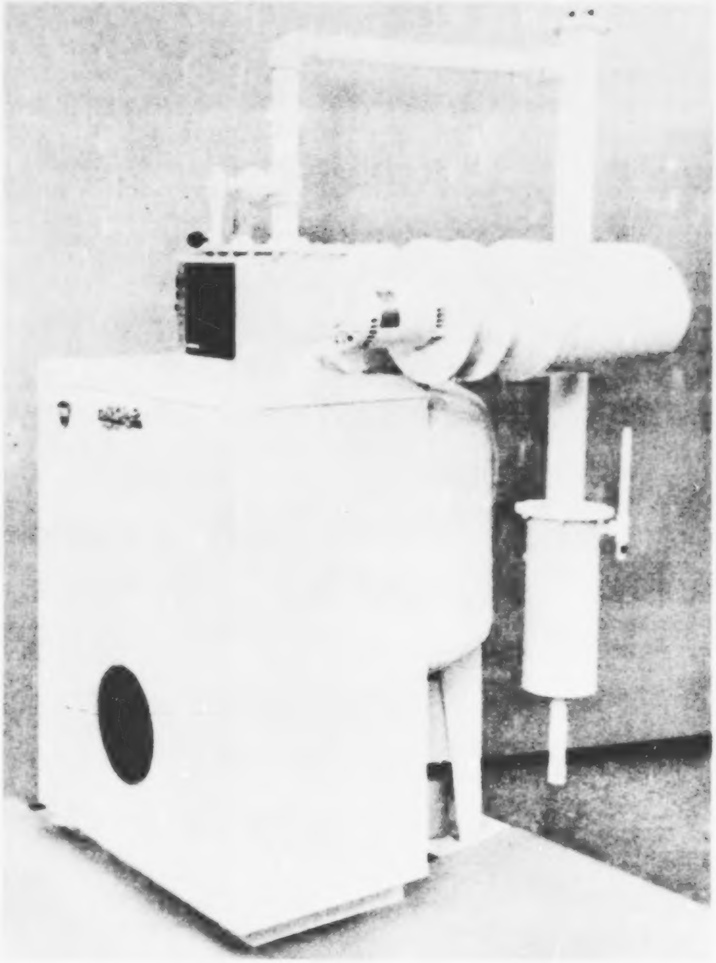


Figure 6-14 Small Cabinet-Enclosed Solvent Recovery Unit, 700 ft^3/min Capacity, Steam Regeneration. Courtesy of Hoyt Manufacturing Corporation.

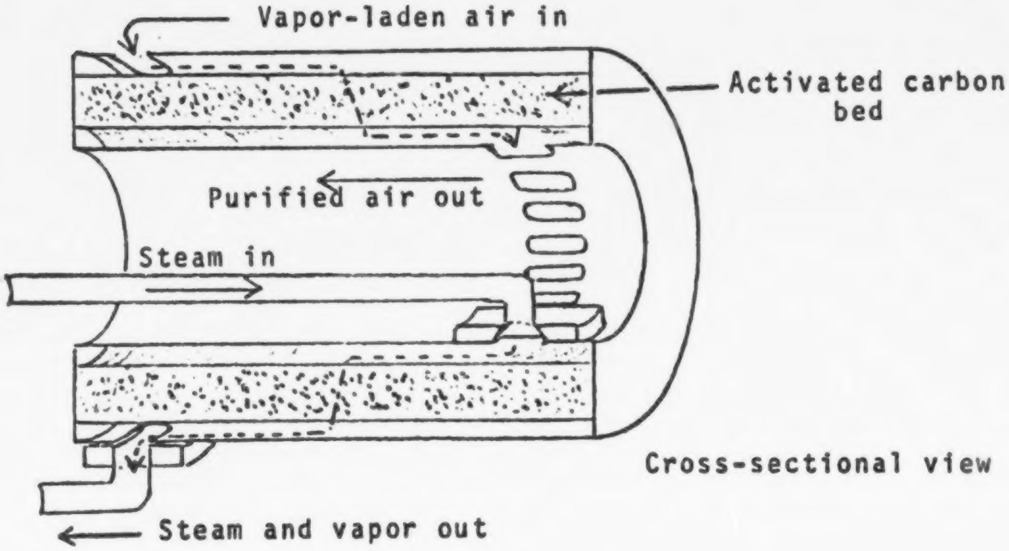
stream then passes through one of the carbon adsorbers. The overall cycle time is 14 min, but programmed to operate different lengths of time on extracting and tumbling depending on clothing to be cleaned.

In the 8-lb machine the clothes drying airflow is about 100 ft^3/min. The adsorbers are 16 in. diameter and 28 in. in length and contain up to 100 lb of 4 to 6 mesh pelletized activated carbon. Steam regeneration of the carbon usually starts after the fourth clothes cleaning cycle and proceeds over several cycles. The Freon TF-steam vapor is condensed, separated by decantation and the Freon TF run into storage for future use without any additional treatment required.

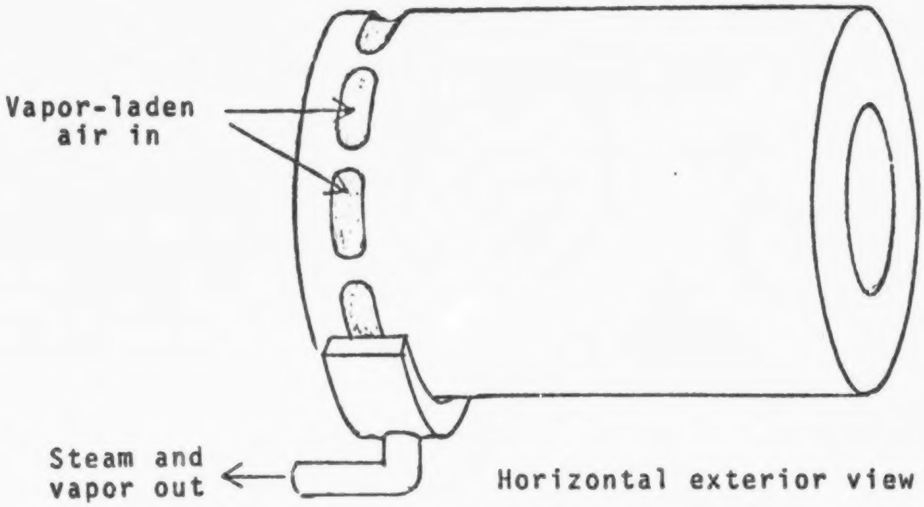
Moving Bed Systems

The concept of the moving bed system is illustrated in Figure 6-15. The rotary component of the system consists of four coaxial cylinders. The outer cylinder is impervious to gas flow except at the slots near the left end. They serve as impure air inlet ports where they are shown uncovered and as steam-vapor outlet ports as shown at the lower left end of the rotary. The carbon bed is retained between two cylinders made of screen or perforated metal and also segmented by partitions placed radially between the two cylinders. The inner cylinder is again impervious to gas flow except at the slots near the right end of the rotary. These slots serve as outlet ports for the purified air and inlet ports for the regenerating steam. On each rotation of the rotary, each segment of the bed undergoes adsorption and regeneration. The desorbed solvent can then be separated from the steam by decantation or distillation.

Because of the continuous regeneration capability of the rotary bed, a more efficient utilization of the carbon is possible than with stationary bed systems. In most solvent recovery operations the adsorption zone is between 3 and 4 in. The unsaturated carbon bed in front of the adsorption zone and the saturated bed behind it are idle but add to the bulk of the system and increase airflow resistance through the bed. In deep beds of 12 to 36 in., as required in the stationary bed systems for regeneration time, a large portion of the bed is idle at any one time. By continuous regeneration, the regeneration time for each segment of the bed is shortened and thereby shorter bed lengths can be used. This leads to two advantages: (1) more compact system and (2) reduced pressure drop.



Cross-sectional view



Horizontal exterior view

Figure 6-15 Continuous Rotary Bed, Based on Sutcliffe Speakman Co., LTD Illustrations, 66 Palmer Ave., Bronxville, N.Y.

The disadvantages are those associated with wear on moving parts and maintaining seals in contact with moving parts. The use of shorter beds also decreases the steam utilization efficiency.

Fluidized Bed Systems

Figure 6-16 shows a flow diagram for a fluidized bed solvent recovery system, based on illustrations from Avery (1969). The carbon is recirculated continuously through the adsorption-regeneration cycle. The spent carbon, saturated with solvent, is elevated to the surge bin and then passed down into the regeneration bed where it is contacted to an upward flow of steam. The regenerated carbon is then metered into the adsorber where the carbon traverses nine beds while fluidized with the upward flow of the vapor-laden air. Air velocity of 240 ft/min is required to cause fluidization of the bed. In both the regeneration and adsorption phases the carbon is moved countercurrent to the gas or vapor.

The countercurrent movement increases the efficiency of regeneration, i.e., the steam-to-solvent ratio is less than for a stationary bed under otherwise comparable conditions. For a number of solvents, Avery reports 40% to 50% less steam required for their recovery. In addition to the beneficial effects of the countercurrent movement, the bed length can be increased to further improve the steam utilization.

The countercurrent movement also increases the effective use of the carbon; more solvent can be recovered with less carbon than with stationary or rotary bed systems. By adjustments or balance of the carbon and solvent input rates, the total carbon in the adsorber can be made part of the adsorption zone but have the carbon reach saturation in the lowest bed just before it is discharged into the elevator. Very little of the carbon is then idle, hence the maximum utilization is made of the carbon.

The fact that the carbon has reached saturation when delivered to the regeneration phase is another factor in the reduced steam requirement. In this respect the fluidized bed system offers the most favorable conditions for solvent desorption while the rotary bed offers the least favorable. In the rotary bed operations, the carbon moved into the regeneration phase has reached the lowest state of saturation in the three systems.

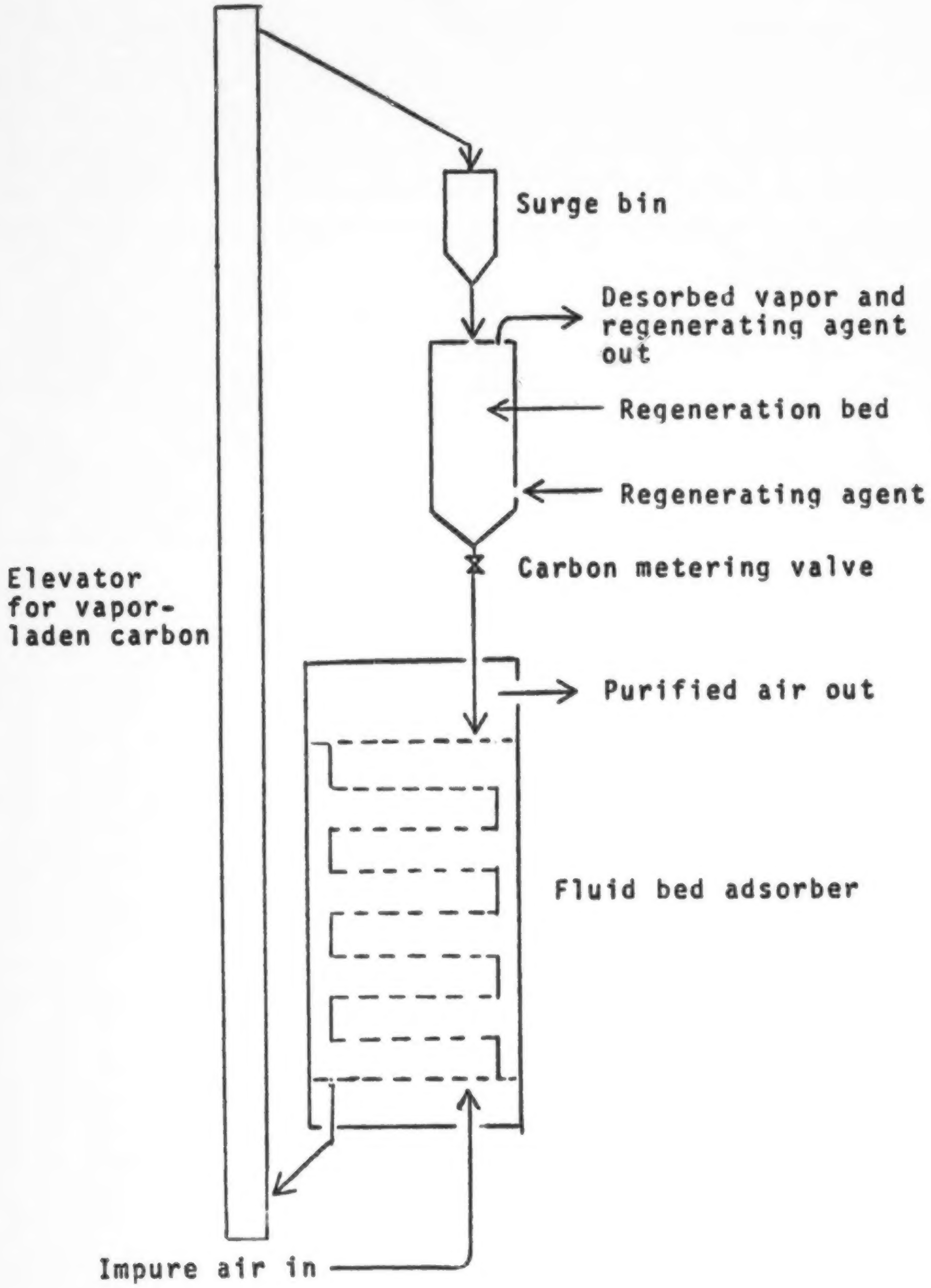


Figure 6-16 Fluidized Bed Solvent Recovery System

In the operation of this particular unit, Avery reported penetration of 100 ppm when carbon disulfide was being adsorbed at 1,000 ppm and 100 ppm when acetone was being adsorbed at 1,700 ppm. This was a continuous penetration and not the temporary penetration that might occur from a stationary bed just before it is taken off stream. By increasing the number of beds, the penetration from the fluidized bed system can be decreased to any desired level but with an increased pressure drop penalty.

When large air volumes are treated and available space for the installation is at a premium, the smaller size and also the lower initial cost are definite advantages over the stationary bed system.

A serious disadvantage is high attrition losses of the carbon caused by the fluidization of the beds. Because of the attrition, filtration of the effluent airstream may be required. Influent airstream need not be filtered since no plugging of the fluidized beds can occur.

Carbon Resorb Systems, New Technology

General Discussion

Most of the present adsorption technology has been directed toward goals other than the reduction of pollutant vapor emissions into the atmosphere. In complying with one of the objectives of this study, attention has been directed toward developing new means or adapting the present technology for pollutant emission control. To attain this goal a detailed study was made to determine the capabilities of available adsorbents and to explore possible modifications to presently used adsorption systems to adapt them for pollution control under the wide variety of conditions under which pollutants are emitted.

The area open to technical advances in package sorbent systems for pollution control appears to be in modification of the systems and operating procedures used in solvent recovery. Since the primary objective is pollution control rather than solvent recovery, the modified systems are referred to in this report as carbon resorb systems. As in solvent recovery, two phases of the operating cycle are adsorption and regeneration, but also includes an additional operation, the disposal of the desorbed pollutant. An important requirement of the disposal procedure is that it does not cause repollution of the air or waterways.

The main departure in the regeneration of carbon resorb systems is the use of heated noncondensable gases in place of steam. As the influent concentration decreases, the amount of steam required per regeneration also increases. At low concentrations the amount of steam required relative to the amount of pollutant desorbed is so large that separation of pollutant from the steam becomes impractical. The extent of pollutant dilution in steam condensate was calculated for a 3,000 ft^3/min capacity solvent recovery system when used to clean an airstream containing pollutants at 10 ppm concentration and regenerated with steam. The results of the calculations are summarized in Table 4-XX.

The three organic compounds listed in the table were selected as representatives for the wide variety of solvents or pollutants that require control. 4-Methyl-2-pentanone is representative of strongly adsorbed compounds which are completely oxidizable to CO_2 and H_2O and are slightly soluble in water. Propanone is representative of weakly adsorbed compounds, completely oxidizable, and completely miscible with water. Trichloroethene is intermediate in adsorbability, is slightly soluble in water, but on oxidation yields HCl, a potential air pollutant.

The high steam-to-solvent ratios, as given in the last column of the table, for each of these compounds mean that many pollutants cannot be economically separated from the steam condensate. Those that are soluble or even slightly soluble will be completely dissolved and separation by distillation would be too costly. Disposal of polluted steam condensate into the sewer can also lead to further pollution of the waterways. Means are proposed by which this problem can be avoided.

Compounds such as tetrachloroethene, aliphatic and naphthenic hydrocarbons above C_6 are reported to be insoluble in water. Separation of compounds of this type appears economically possible by decantation.

When a noncondensable gas is used as regenerating agent, the desorbed pollutant may be disposed of by several means. If it is completely oxidizable to CO_2 and H_2O it can then be immediately destroyed by incineration upon desorption from the carbon. If it has recovery value, or is noncombustible or would repollute the air on incineration, the desorbed pollutant may be readsorbed on a small secondary carbon bed and recovered from it by conventional steam regeneration or it may be recovered from the regenerating gas by condensation.

These three procedures for immediate disposal or recovery of the pollutant can be incorporated into any of the three solvent recovery type systems described earlier in this chapter, i.e., stationary bed, moving bed and fluidized bed systems.

Other aspects of the adsorption and regeneration phases have also been examined to determine possible means for improved utilization of the carbon and regenerating agent.

The various concepts as incorporated into various operational systems can be identified according to the mode of regeneration and disposal of the desorbed pollutant. These are:

Heated air or inert gas regeneration followed by thermal or catalytic incineration of the desorbed (completely combustible) pollutant,

Heated air or inert gas regeneration of primary bed followed by readsorption of desorbed pollutant on a secondary bed and steam regeneration of secondary bed to recover pollutant,

Heated air or inert gas regeneration with desorbed pollutant (or solvent) condensed at lowered temperature and recycle of uncondensed vapors through carbon bed,

Two-stage adsorption with stationary bed system and single-stage regeneration,

Two-stage regeneration with stationary bed system and single-stage adsorption,

Regeneration by pressure reduction,

Continuous or intermittent removal of spent carbon from adsorption system followed by high temperature steam reactivation of the carbon on plant site.

These systems are described in the following text with statements made regarding advantages and disadvantages. The descriptive portion is followed by economic analysis of solvent recovery and some of the proposed systems. Cost comparisons are given with the competing systems: catalytic and thermal incinerations.

Gas Regeneration with Incineration

For pollutants that are completely oxidizable, regeneration with an inert, noncondensable gas followed by incineration of the desorbed pollutant is a procedure that offers a relatively low cost regeneration and simultaneously effects complete disposal of the pollutant. In this case the carbon bed acts as a concentrator. The incinerator can then be relatively small requiring little additional expense to operate.

To show the manner in which the system would operate, the following sample calculations have been worked-up for 4-methyl-2-pentanone from data given in Table 4-XX. At 0.025 lb/lb operating capacity, 37.5 lb of the solvent are adsorbed on the carbon from 1,500,000 ft^3 of air passed through the bed over a period of 82 hr at 3,000 ft^3/min flow and 10 ppm concentration. The regeneration can be accomplished with 37,000 ft^3 of inert gas (near 28.9 lb/mol) at 302°F regeneration temperature, yielding an effluent mixture of 4,000 ppm mean solvent concentration. (The regeneration data are obtained from predetermined curves of type shown in Figures 4-22, -23 and -24.) The size of the incinerator depends on the regeneration time. For a two-hour regeneration, the incinerator would be sized for a 300 ft^3/min flow rate. This is 10% of the 3,000 ft^3/min flow capacity of the carbon resorb system or incinerator if the vapors were incinerated directly at the 10 ppm. In addition, direct incineration would require a considerable amount of fuel to heat the air to the incineration temperature. Incineration of the carbon bed effluent would require very little fuel since the air volume is much smaller and the high concentration of the pollutant supplies the major part of the fuel requirements.

By use of a noncondensable gas, rather than steam, the heating cost of the regenerating gas is considerably less. The above regeneration requires 2,400 lb of steam, which at 0.1¢/lb costs $2.40. Noncondensable gas regeneration requirement is 2,700 lb, which at 0.005¢/lb, costs $0.13. Steam cost is about $0.01/hr per 1000 ft^3/min flow. At the 10 ppm pollutant concentration level where regenerations are not frequent, the steam and definitely the noncondensable gas costs are not significant relative to the other operating costs which can add up to at least $0.25/hr per 1000 ft^3/min or to $0.55/hr per 1000 ft^3/min, the more probable cost level.

As the pollutant concentration increases, the advantages of using a noncondensable gas regeneration-incineration combination decrease. When the pollutant is a solvent of recovery value, the incineration of the solvent would constitute an increasingly greater loss of a valuable product. At higher pollutant concentrations and more frequent regenerations, increasingly larger incinerators are required. At concentrations approaching 25% LEL, the required incinerator capacity is the same as for direct incineration. At concentrations between 700 to 1000 ppm, the cost of the carbon resorb with incineration approach those of direct incineration; see Figure 6-31.

The general concept of carbon resorb and incineration systems combination has been investigated by Mattia (1969, 1970). A flow diagram of the proposed process is presented in Figure 6-17. Adsorption proceeds in the same manner as in solvent recovery, but regeneration is accomplished by recycle of gas through the carbon bed and incinerator, which can be either thermal or catalytic. The regenerating gas is initially air but on passing through the adsorber and incinerator it becomes converted to a mixture low in oxygen with increased carbon dioxide and water vapor. Make-up air is added to the incinerator to supply enough oxygen to burn the pollutants desorbed from the carbon bed. To avoid damage to the carbon from over-heated regenerating gas, a cooler is required in the recycle line. To maintain proper regeneration temperatures and flow rates, instrumentation and closer controls are required than needed for solvent recovery. The process is recommended for fairly large air volume control, 10,000 ft^3/min and larger.

In the operation of this process, a balance is maintained between the time period for the adsorption phase and regeneration phase to attain the best overall efficiency. As an example of operating conditions, a process may be designed to adsorb a pollutant at 200 ppm concentration in 90 min and flow velocity near 100 ft/min. Regenerating gas flow and temperature are adjusted to regenerate the carbon in 75 min allowing 15 min for bed cooling. Regenerating gas flow rates are variable from 2% to 10% of the adsorption flow rate. Temperatures are adjusted to produce the desired rate of desorption. A 300°F temperature was considered maximum. The carbon bed depths are 4 to 8 in., much shorter than in solvent recovery, to bring the service time to the one hour level at the lower concentrations.

It should be noted that the regenerating gas flow indicated in Figure 6-17 is in the same direction as the adsorption flow, instead of reversed as normally done in

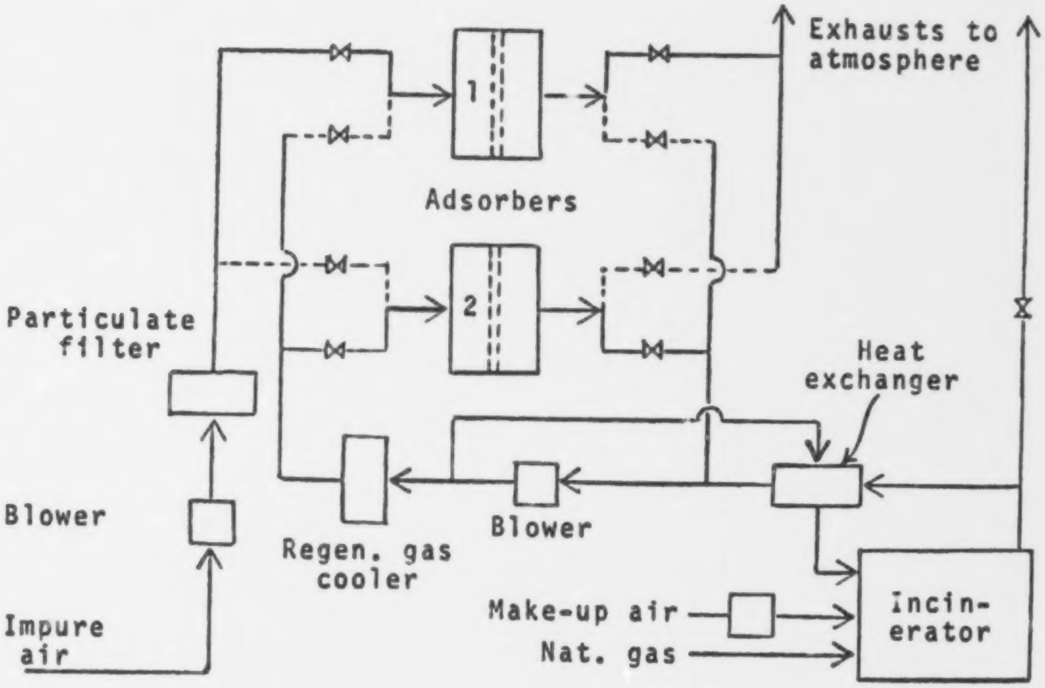


Figure 6-17 Air Pollution Control System Utilizing Carbon-Resorb with Gas Regeneration and Incineration of Desorbed Pollutants. (from Mattia, 1970)

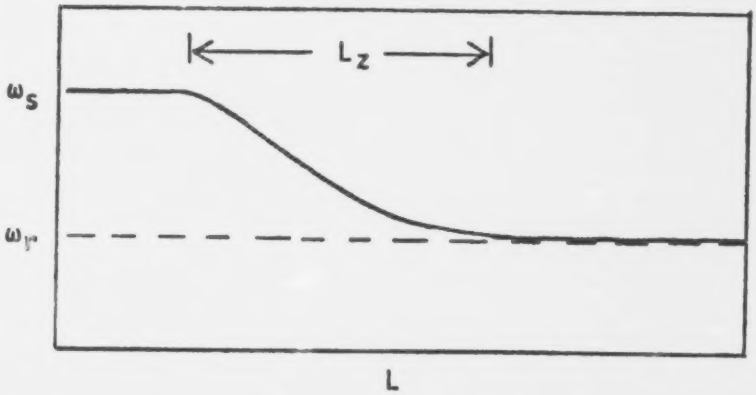


Figure 6-18 Adsorption-Phase Profile After Carbon Bed Has Been Regenerated, When L is 4 to 8 in., and ω_r is Residual Capacity.

solvent recovery operations. This procedure leaves an adsorbed-phase residue in the carbon bed that extends to the effluent end. This is shown in Figure 6-18. Because of the residual capacity, immediate penetration occurs in the adsorption phase at a low concentration. The penetration concentration is the concentration in equilibrium with the residual capacity. By increasing the operating capacity, $\Delta\omega = \omega_S - \omega r$, the amount of penetration can be decreased to lower levels. The process is also operated with reverse flow (Mattia, 1969). In this case the adsorbed phase profiles are similar to those illustrated in Figure 4-21.

Another operational characteristic that should be noted is that the pollutant concentration in the regenerating gas stream is not constant but varies with regeneration time in a manner shown in Figure 6-19. This variation in concentration produces effects in the disposal operation which must be compensated by corrective measures. In incineration, it is basically a variation in fuel input; natural gas input rate must be adjusted to maintain the incinerator temperature at the effective level over the total regeneration phase.

Gas Regeneration with Secondary Adsorption

When the pollutant, adsorbed from a low concentration airstream, contains halogens, NO_x and SO_x groups, incineration of the desorbed pollutants would repollute the air with acids of these groups. Other means are required to dispose of the desorbed pollutants than the incineration method described in the preceding text. One of the methods that is feasible on theoretical grounds utilizes a secondary carbon adsorber operating as a solvent recovery unit for the effluent regeneration gas stream.

The manner in which the system would operate can be demonstrated with the sample calculations used in the preceding text on Gas Regeneration with Incineration. In the adsorption-desorption process the 4-methyl-2-pentanone is removed from an air volume of 1,500,000 ft^3 at 10 ppm concentration and concentrated into an air volume of 37,000 ft^3 at a mean concentration of 4,000 ppm. The secondary adsorber is then required to recover 37.5 lb of 4-methyl-2-pentanone every 82 hr from 37,000 ft^3 of gas volume at 4,000 ppm mean concentration.

Since the desorbed solvent concentration varies over the regeneration time period in a manner shown in Figure 6-19, the estimating procedure for determining the carbon bed size would be quite involved if the changes in concentration were taken into consideration. A very approximate estimate of the bed size may be attained if the 4,000 ppm mean concentration is assumed constant over the regeneration time period.

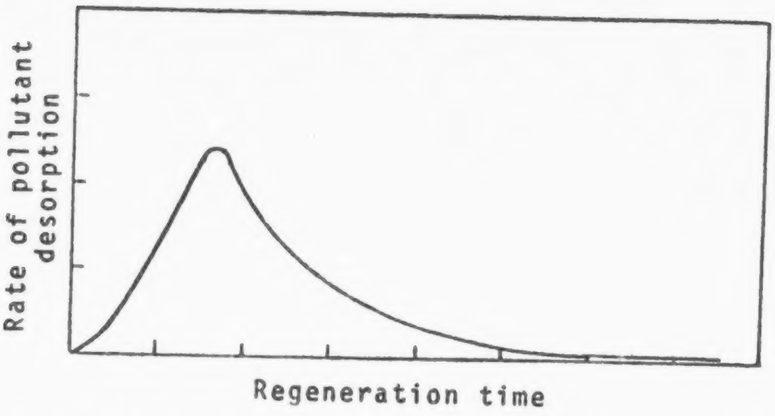


Figure 6-19 Pollutant Desorption Rate Variation with Regeneration Time

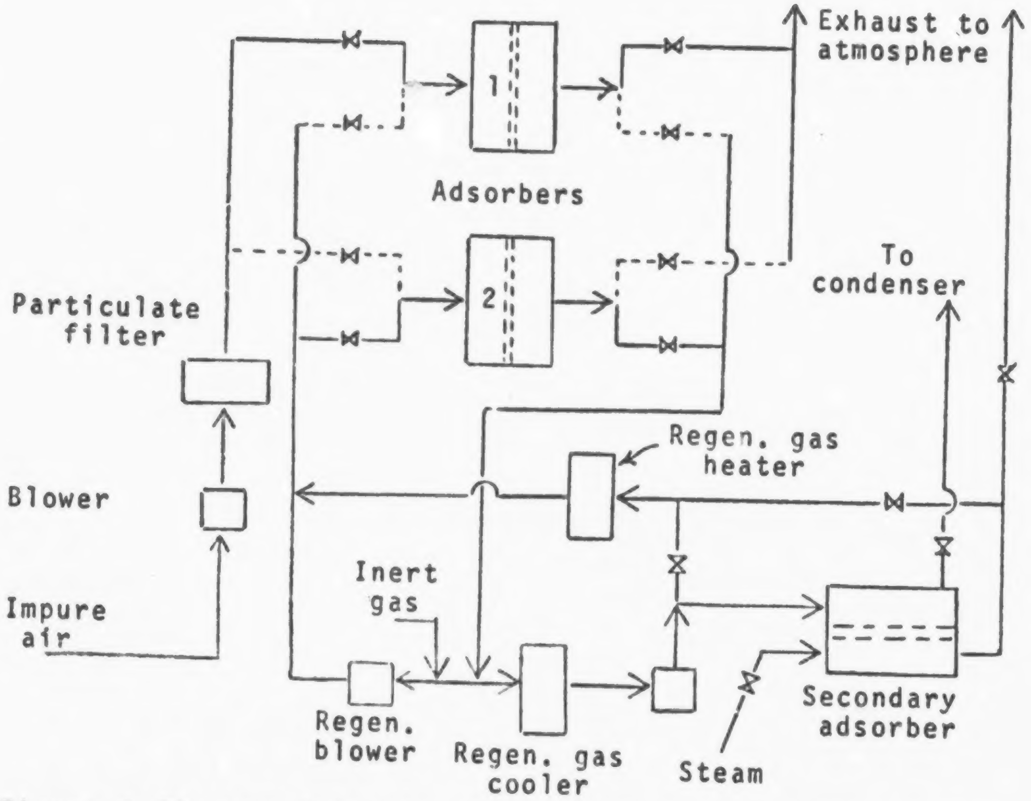


Figure 6-20 Air Pollution Control System Utilizing Carbon-Resorb with Gas Regeneration and Secondary Adsorber for Desorbed Pollutants. (from Mattia, 1970)

The parameter that greatly affects the required bed size is the choice of steam-to-solvent ratio that the adsorber is to operate at. If operations were chosen at steam-to-solvent ratio of 3.0, the required operating capacity is 0.08 lb/lb for the saturated layer. The estimated carbon bed weight is approximately 500 lb or 33% of the 1500 lb for the primary bed. By increasing the steam-to-solvent ratio to 6.0, the required operating capacity is increased to 0.14 lb/lb. The estimated carbon weight reduces to 300 lb or 20% of the primary bed weight. The details of the calculations for the latter estimate are given in Appendix E, page E-24.

By reducing the primary bed thickness and thereby, also, the adsorption-regeneration cycle time, the secondary bed size can be further reduced. When the adsorption and regeneration phases for the primary adsorbers are balanced, two secondary adsorbers may be used, also, operating alternately on adsorption and regeneration.

Figure 6-20 presents a flow diagram of the proposed system as engineered by Mattia (1969, 1970). Inert gas (could be flue gas) is fed into the system at the start of the regeneration and recycled through the primary and secondary adsorbers. The regenerating gas from the secondary adsorber passes through the surface heater where it is heated to an elevated temperature. On blending with a side-stream being recirculated through the primary adsorber, the temperature of the combined gas stream on entering the primary adsorber is near 300°F. A part of the vapor-laden gas stream from the primary adsorber passes through the cooler where it is cooled down to 100°F, or lower, before being directed through the secondary adsorber.

At increasingly higher pollutant concentrations the advantages in using secondary adsorbers decrease and direct regeneration of the primary adsorber increase.

Gas Regeneration with Condensation and Recycle

A third proposed method utilizes a condenser to recover the desorbed pollutant vapor from the regenerating gas.(1) By operating the condenser at a very low temperature an almost complete condensation of most pollutants could be realized, but to avoid costly refrigeration a more economical approach is to operate the condenser at a readily attainable higher temperature and recycle the uncondensed vapor through the on-stream adsorber. As the condenser temperature is raised the amount of recycle becomes larger. The limiting factor is the adsorptive capacity of the carbon bed, hence operation of the process at practical condenser temperatures is only attainable with the less volatile pollutants. The increase in regenerating gas to handle the recycled vapor is small and is not a significant factor in the operating cost.

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(1) Proposed by B.B. Carr, MSA Research Corp., Evans City, Pa.

Figure 6-21 presents a flow diagram that illustrates the general scheme of this type of operation. An inert regenerating gas is prepared and heated by burning natural gas or any other completely oxidizable fuel. The regenerating gas is then cooled to near 300°F and passed through the off-stream adsorber, in this case Adsorber 2. The vapor-laden hot effluent from Adsorber 2, on passing through the condenser, is cooled and, if the dew point is reached, a portion of the vapor condenses. The uncondensed vapor and regenerating gas continue their flow into the impure air stream and to the on-stream Adsorber 1 where the recycle vapor is readsorbed. During the desorption phase of Adsorber 1, the vapors from the impure air and recycle gas streams are both desorbed but at a higher concentration and in a slightly larger regenerating gas volume than during the initial start-up cycle. On each successive adsorption-regeneration cycle the amount of vapor recycled increases until either the adsorptive capacity of the carbon bed is exceeded or the condensation rate equals the pollutant vapor input rate.

To gain further insight into the manner in which this system operates, calculations were made using the carbon-resorb system as described in the prior text under Gas Regeneration with Incineration and Gas Regeneration with Secondary Adsorption. In the initial cycle of the adsorption-desorption process the 4-methyl-2-pentanone is removed from an air volume of 1,500,000 ft^3 at 10 ppm concentration and concentrated into a gas volume of 37,000 ft^3 at a mean concentration of 4,000 ppm. On the second and successive cycles, these gas volumes and concentrations change until a steady state is reached. At steady state operation the condenser removes 37.5 lb of 4-methyl-2-pentanone from the regenerating gas stream with the uncondensed balance returned to the on-stream adsorber.

The regeneration of the off-stream adsorber is started on the 80th hr and continued to the 82nd hr over a 2-hr regeneration period. By regenerating the off-stream adsorber near the end of the service time, the recycled vapor is readsorbed in the influent end of the on-stream adsorber.

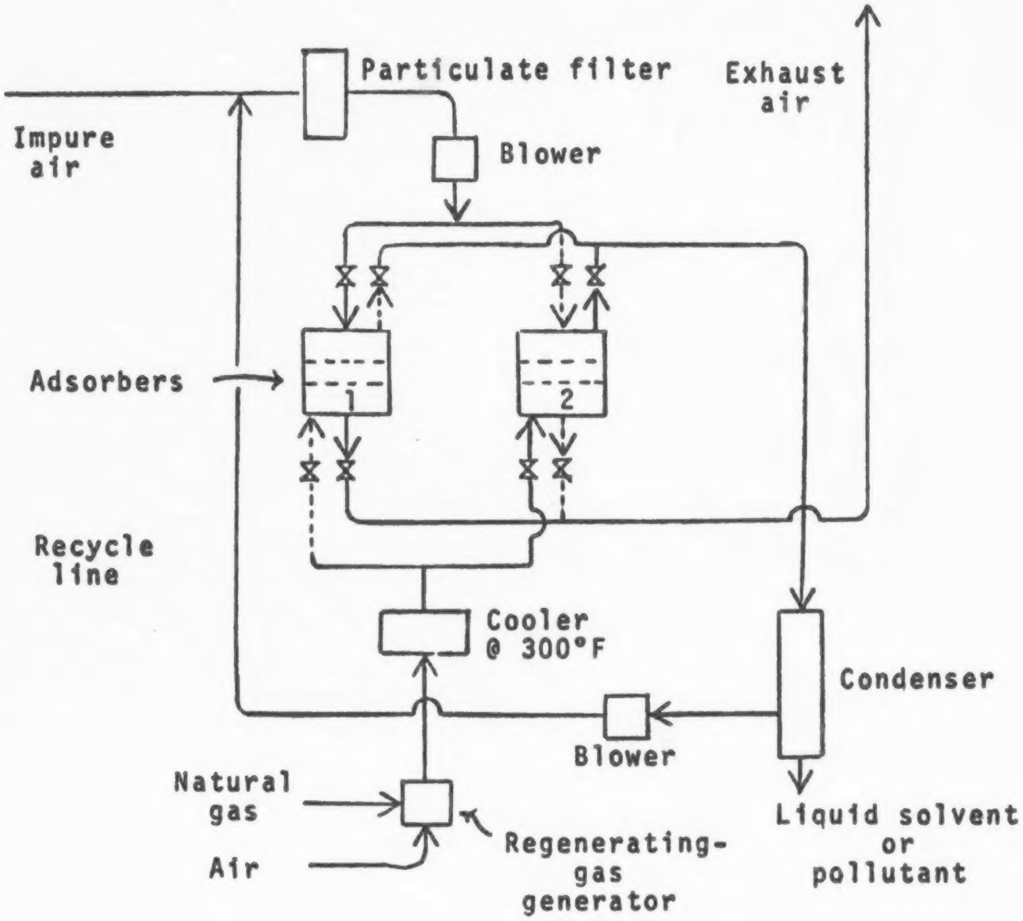


Figure 6-21 Air Pollution Control System Utilizing Carbon-Resorb with Gas Regeneration, Condensation, and Recycle of Uncondensed Vapor.

The readsorbed vapor is now in a favorable position for ease of desorption when regenerating gas flow is in the reverse direction.

The concentration of the desorbed vapor in the regenerating gas stream varies in a manner indicated in Figure 6-19. This concentration variation has an affect on the operation of the condenser and also on the readsorption of the recycled vapors. To simplify the calculations the concentration was assumed constant at the mean level.

Two estimates were made, one with the condenser operated at 77°F and the other at 32°F. In each case the initial flow to the adsorber is 3,000 ft^3/min at 10 ppm concentration. When the condenser is operated at 77°F, the steady state is attained on the 6th cycle. At the steady state, the following operating conditions prevail during the 2-hr regenerating time period:

F to adsorber = 3,330 ft^3/min
C_i to adsorber = 940 ppm
F to condenser = 330 ft^3/min
C_e to condenser = 13,000 ppm
Weight of vapor recycled = 95.2 lb/cycle
Weight of vapor condensed = 37.5 lb/cycle

When the condenser is operated at 32°F, the steady state is attained on the 2nd cycle. At the steady state the following conditions prevail during the 2-hr regenerating time period:

F to adsorber = 3,310 ft^3/min
C_i to adsorber = 160 ppm
F to condenser = 310 ft^3/min
C_e to condenser = 5,500 ppm
Weight of vapor recycled = 15.1 lb/cycle
Weight of vapor condensed = 37.5 lb/cycle

During the service time up to 80 hr, F to adsorber is still 3,000 ft^3/min and C_i is 10 ppm.

For the system operating at 77°F condenser temperature, 132.7 lb of vapor are adsorbed by the carbon every 82 hr of which 95.2 lb are recycle vapor and 37.5 lb are from the atmosphere. For the system operating at 32°F condenser temperature, the carbon adsorbs 52.6 lb of vapor of which 15.1 lb are recycle vapor and 37.5 lb are from the atmosphere. Detailed calculations for the 32°F condenser operation are given in Appendix E, page E-27.

Figure 6-22 presents adsorbed-phase profiles showing the probable status at the start of the regeneration phase and at the end of the adsorption phases for the process when operated at the two condenser temperatures. The adsorptive capacity is measured in lb/in. of bed length; hence the product of capacity times bed length gives a direct measure of pounds adsorbed under any curve.

The broken-line profile represents the status just after regeneration has been completed. The mean capacity $\omega r = 8.88$ lb/in. The area under the curve, $W_r = 189.5$ lb, is the total amount remaining on the carbon after any cycle. The profile designated by 10 ppm represents the status at the end of the adsorption phase when no recycling is done. In this case, $\omega_s = 10.65$ lb/in. and the area under the curve represents the adsorbed amount, $W_s = 227$ lb. The difference,

$$W_s - W_r = 227 - 189.5 = 37.5 \text{ lb/cycle},$$

is the amount of pollutant vapor desorbed or removed from the atmosphere.

When the vapor is recycled from the 32°F or 77°F condenser, the profile as indicated is superimposed on the 10 ppm profile. The area between the 10 and 940 ppm profile represents 95.2 lb recycle vapor and the area between 10 and 160 ppm, 15.1 lb.

Theoretically, the process is feasible for pollutants of V_m near or larger than 140 cm^3liq/mol. Pollutants of lower V_m would require lower condenser temperatures to avoid exceeding the carbon capacity with the recycle vapor. When the concentration is high enough, recycle is no longer necessary; direct steam regeneration again becomes feasible. Very low molecular weight pollutants cannot be recovered by this process unless the input concentration is quite high or the condenser is operated at a very low temperature.

Two-Stage Stationary Bed System

This system is intended for control of pollutants adsorbed in the 10 to 100 ppm concentration range. It requires two adsorbers or carbon beds on-stream in series. The first carbon bed, on the airstream influent end, is designated as the first stage and the second bed the second stage. For

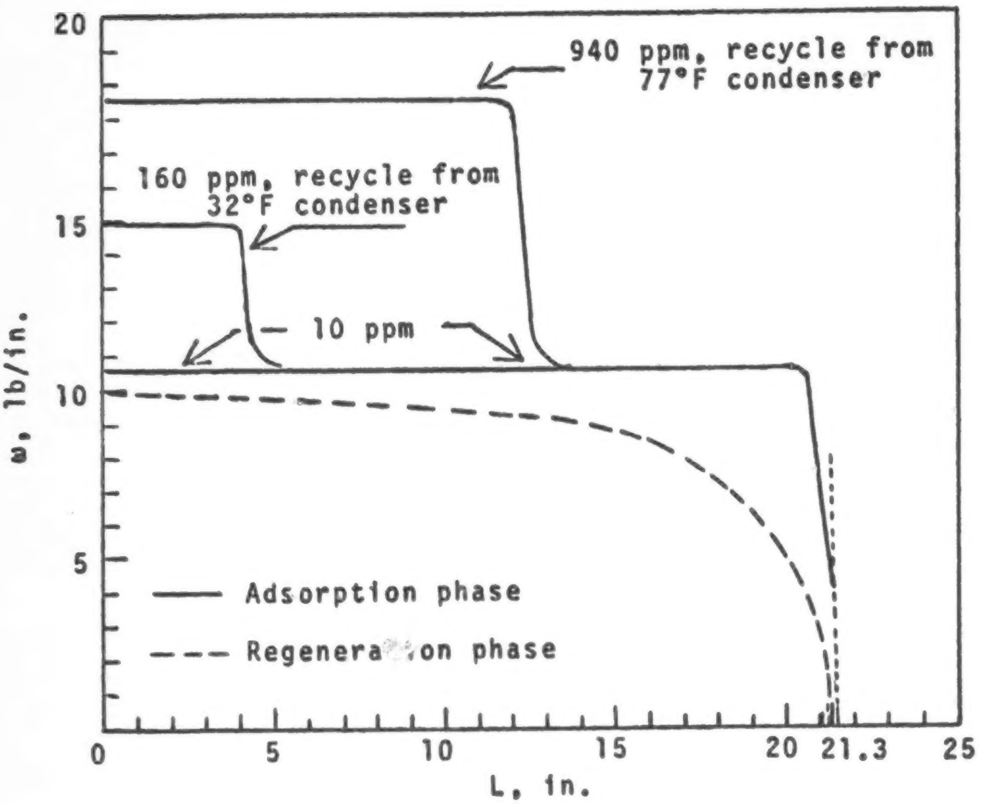


Figure 6-22 Adsorbed-Phase Profiles at the End of Adsorption and Regeneration for a Gas Regeneration-Condensation-Recycle Process, $L_t = 21.3$ in.

best efficiency the bed lengths should be equal to or slightly longer than the adsorption zone length. When adsorption zone has moved into and completely occupies the second stage bed, the first stage bed has become completely saturated and is taken off-stream for regeneration by any one of the means previously described. The second stage bed is moved into the first stage position and a third carbon bed, previously regenerated, is moved into the second stage position. The three carbon beds are moved consecutively through the second and first stages of the adsorption phase and then through the regeneration phase.

The flow diagram in Figure 6-23 shows the essential components of the two-stage system. At the particular time period depicted by the diagram, the airstream is passing through Adsorbers 1 and 2 in succession while Adsorber 3 is being regenerated. When the vapors begin to penetrate Adsorber 2, Adsorber 1 has become saturated with vapor and is taken off-stream for regeneration and Adsorber 3 becomes the second stage and Adsorber 2 the first stage.

This system approximates the countercurrent contacting of the carbon and gas phase, as occurs in the fluidized bed system, and thereby also the effective use of the carbon is increased. However, with the two-stage stationary bed system no carbon loss occurs because of attrition as it does in the fluidized bed system.

The disadvantage is the cost of the additional ducts, valves, more elaborate adsorber construction and controls to operate the valves.

Two-Stage Regeneration of Stationary Bed

Figure 6-19 shows the change in desorption rate with regeneration time for a stationary bed. As the bed becomes heated with passage of regenerating agent, the desorption rate increases to a maximum and then decreases as the pollutant becomes depleted in the bed. In a countercurrent regeneration, the desorption rate does not go through a maximum with regeneration time but settles to a constant rate. Countercurrent regeneration is thereby contributive to better utilization of the regenerating agent; the regenerating agent-to-desorbed pollutant ratio is decreased.

Completely countercurrent regeneration is only possible with systems such as the fluidized bed or moving bed of the "hypersorption-type" described later in this chapter. Much of the benefit of countercurrent regeneration could be gained by multistage regeneration where many stationary beds in series are in the regeneration gas stream. Saturated beds would be intermittently added to the gas effluent end while regenerated beds are removed from the gas influent end. The complexity of the system would economically over balance the benefits from the countercurrent regeneration. It is doubtful that the use of stages greater than two would be economical.

For a two-stage regeneration system, as illustrated by the flow diagram in Figure 6-24, three adsorbers are required. At the particular time period depicted by the diagram, Adsorber 1 is on the adsorption phase while Adsorbers 2 and 3 are on the regeneration phase. Adsorber 2 is in the Stage 2 position and

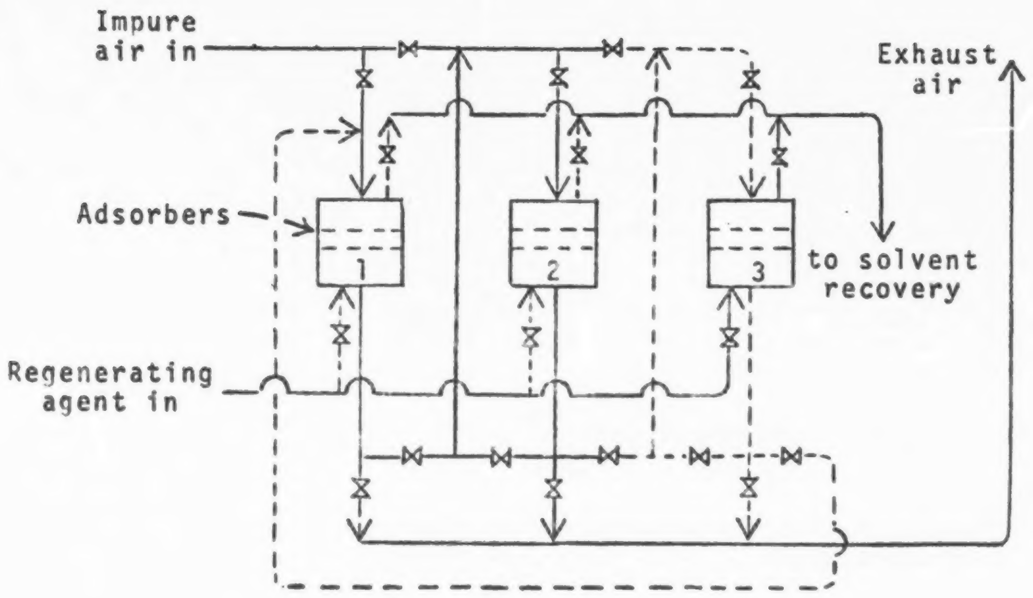


Figure 6-23 Two-Stage Stationary Bed System

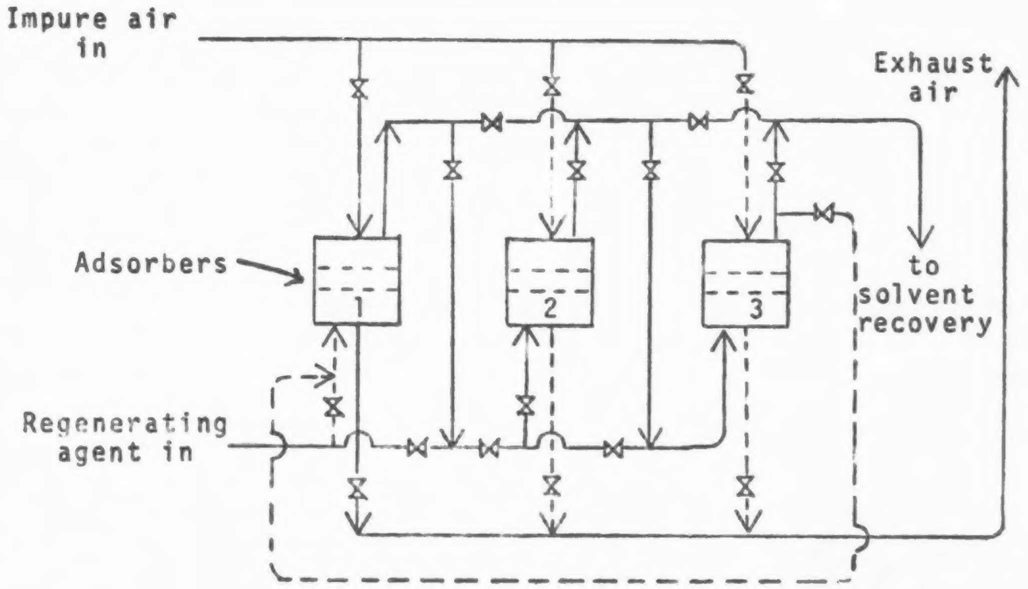


Figure 6-24 Stationary Bed with Two-Stage Steam Regeneration

is in the influent end of the regeneration gas stream and Adsorber 3 is in the Stage 1 position. When vapors begin to penetrate Adsorber 1 it is taken off-stream and connected to Stage 1 position on regeneration. Adsorber 3 is moved from Stage 1 to Stage 2 position and Adsorber 2 goes on-stream on the adsorption phase.

The desorption rate from a two-stage regeneration will fluctuate between maxima and minima with regeneration time. The various pollutant disposal methods will operate more efficiently than when operated in conjunction with a dual stationary bed system.

The disadvantage is the cost of the additional ducts, valves, more elaborate adsorber construction and controls to operate the valves.

Regeneration by Pressure Reduction

When a process is operated at above atmospheric pressure, advantage can be taken of the higher pressure in the adsorption-regeneration cycle. The adsorption increases with increased total pressures since the pollutant concentration increases in the same proportion. Conversely, on releasing the pressure the vapors adsorbed at the higher pressure are released. A small amount of sweep gas at ambient or elevated temperature is then required to accelerate the removal of the vapors from the carbon bed. Table 6-II presents estimated capacity figures that show a $\omega_S = 0.029$ lb/lb at 8 atm pressure during the adsorption phase and when pressure is released to 1 atm, ω_S reduces to 0.014 lb/lb. The operating capacity is then 0.015 lb/lb. The large disadvantage is the initial cost of the heavy construction required for the adsorber tank and valves.

Table 6-II Effect of Pressure on Adsorptive Capacity of Carbon for Propanone, 10 ppm Concentration

Pressure, atm	C_i, lb/ft^3	A	ω_S, lb/lb
1	1.48×10^{-6}	18.0	0.014
2	2.96×10^{-6}	16.8	0.016
4	5.92×10^{-6}	15.5	0.023
8	1.18×10^{-5}	14.3	0.029

Multistage with Bed Displacement

This type system is illustrated in Figures 6-25 and -26. Figure 6-25 shows the inverted conical shaped lower bed of the first stage and the upright conical shaped upper bed of the second stage. Additional stages can be added above the second, although advantages accruing from stages beyond the second diminish rapidly. Impure airflow is maintained through the first stage bed until it becomes completely saturated, i.e., in equilibrium with the influent concentration. The carbon of the first stage is then removed through the bottom valve and simultaneously the carbon of the second stage lowers into the first stage position. New or regenerated carbon from the hopper moves into the second stage position. The spent carbon can now be regenerated or reactivated in a separate unit.

The two-stage system illustrated in Figure 6-26, has an operating capacity of 10,000 ft^3/min. The upright tank containing the carbon beds is approximately 8 ft in diameter and 14 ft in height. Each stage contains about 3,400 lb of carbon, mean flow area is about 82 ft^2, and bed thickness is 16 in. The carbon is a pelletized type of 4 to 6 mesh. In this particular application, at a waste water treatment plant, the carbon is displaced in each of the two stages every 134 da. The spent carbon is then activated with steam at a high temperature (over 1600°F) to its original activity. This means that the operating capacity is the total capacity of the saturated layer rather than a fraction of the saturated layer capacity as is the case in solvent recovery operations where steam is used for regeneration.

Service times were estimated for the above described system at 1.0, 10, and 100 ppm concentrations for 4-methyl-2-pentanone and propanone, as representatives of widely divergent pollutants in regard to adsorbability. The details of the calculations are given in Appendix E, page E-31 and the results in Table 6-III.

Table 6-III Service Time for Pollutant Vapors at Varied Concentrations in a Two-stage System with Displacement of Beds

	4-methyl-2-pentanone		propanone	
C_i, ppm	ω_s, lb/lb	t, hr	ω_s, lb/lb	t, hr
1	0.11	2450	0.0047	180
10	0.16	360	0.013	50
100	0.20	45	0.034	13

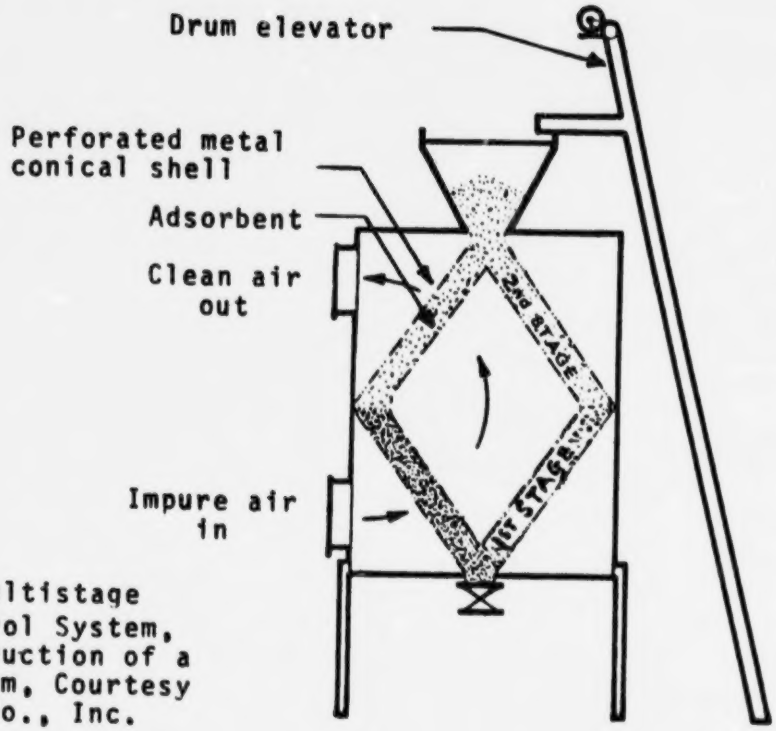


Figure 6-25 Multistage Pollutant Control System, Internal Construction of a Two-Stage System, Courtesy T. Melsheimer Co., Inc.

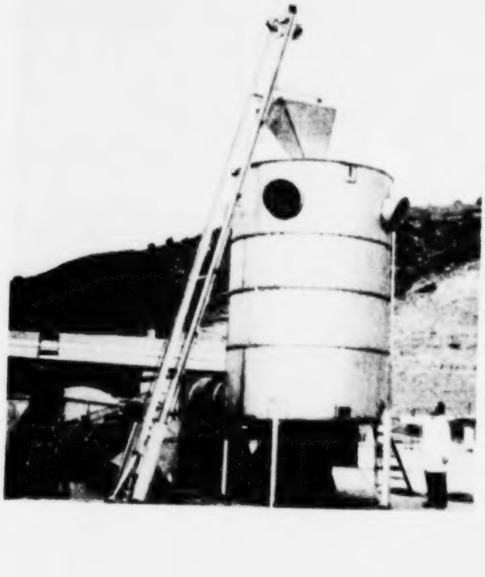


Figure 6-26 Two-Stage Pollutant Control System, 10,000 ft³/min Capacity, Courtesy T. Melsheimer Co., Inc.

This type system offers the most benefits when the pollutants are high molecular-weight types and are emitted at low concentrations. High molecular-weight pollutants, having V_m larger than 190 cm^3liq/mol, are not completely desorbed by the regular steam regeneration procedures as practiced in solvent recovery. Incomplete desorption also occurs when the pollutant can polymerize while in contact with the carbon. Reactivation would then be a frequent necessity and would be a costly operation with the design of equipment used in solvent recovery. The design of this system minimizes the cost of transfer of carbon between the adsorption and activation phases of the operation.

The longest service time calculated for Table 6-III is 2450 hr or 102 da occurring at 1 ppm concentration when the pollutant has the adsorptive properties of 4-methyl-2-pentanone. For the control of low molecular weight pollutants, as represented by propanone, or control of the heavier molecules at 10 ppm and higher concentrations, the service times are much shorter thereby requiring more frequent reactivation of the carbon. The frequency and cost of reactivation is the controlling operating cost which determines the suitability of the system for any given application. Cost estimates of carbon reactivation relative to the amount of air purified show the trend to be expected. The equation used for the estimates is

$$\frac{W_c \text{ reactivated} \times \$/\text{lb for react.}}{t \times [F/1000]} = \$/\text{hr per } 1000 \text{ ft}^3/\text{min.}$$

The estimated costs for three service times selected from Table 6-III are given below when cost of reactivation, reactivation losses and handling are $0.25/lb:

t, hr	$/hr per 1,000 ft³/min
2450	0.034
360	0.23
180	0.47

For the 2450-hr service time the $0.034 reactivation cost is not significant relative to the fixed operating costs, which are generally near $0.50/hr per 1000 ft³/min for carbon-resorb systems. Carbon reactivation costs of $0.47/hr per 1000 ft³/min would make the multistage system noncompetitive with catalytic incineration and possibly with thermal incineration if the airstream is already at an elevated temperature. See Figure 6-31 for estimated operating costs of the different types of systems.

A disadvantage of this system is that adsorbed pollutants containing halogens, nitrogen or sulfur would repollute the atmosphere when desorbed and decomposed during reactivation.

"Hypersorption" System

Figure 6-27 illustrates the "Hypersorption" system as developed by Berg (1947) for the separation of the light hydrocarbon gases: hydrogen, methane, ethane and propane. The hot carbon from the steam regeneration, at the lower end of the column, is gas lifted to the hopper at the top. On passing through the cooler, the carbon is cooled with recycle gas used in the gas lift. This is the least-strongly-adsorbed gas of the mixture. In the adsorption section, the downward moving carbon flows countercurrent to the gas mixture entering the system at the inlet port. The least-strongly-adsorbed gas is partially exhausted from the system at the discharge port and partially as the recycle gas. The more-strongly-adsorbed components of the mixture are carried downward with the carbon through the rectifying section and to the stripper. In the stripper the most-strongly-adsorbed gas is desorbed and leaves the system at the make-gas port. The reflux of the most-strongly-adsorbed gas displaces the next-strongly-adsorbed gas upward in the carbon bed. This gas leaves the system at the side-cut port. The reflux of the next-strongly-adsorbed gas displaces the most-weakly-adsorbed gas upward in the rectifying section and thereby forcing it into the adsorption section.

The adsorption of methane, ethane and propane are quite small even at atmospheric pressure, being of the order of 0.001, 0.01 and 0.20 lb/lb, respectively. The differences are significant so that separation is possible, but, because of the low capacities, frequent adsorption-regeneration cycles are required to attain a practical production rate.

By only moving the carbon and by the countercurrent operation, three beneficial effects are realized:

1. In the regeneration phase only the carbon and adsorbate are heated; no heat is wasted in reheating hardware;

2. Because of the countercurrent flow the full adsorptive capacity of the carbon is utilized; and

3. The transfer of carbon between the adsorptions and regeneration phases is carried out continuously in an efficient manner.

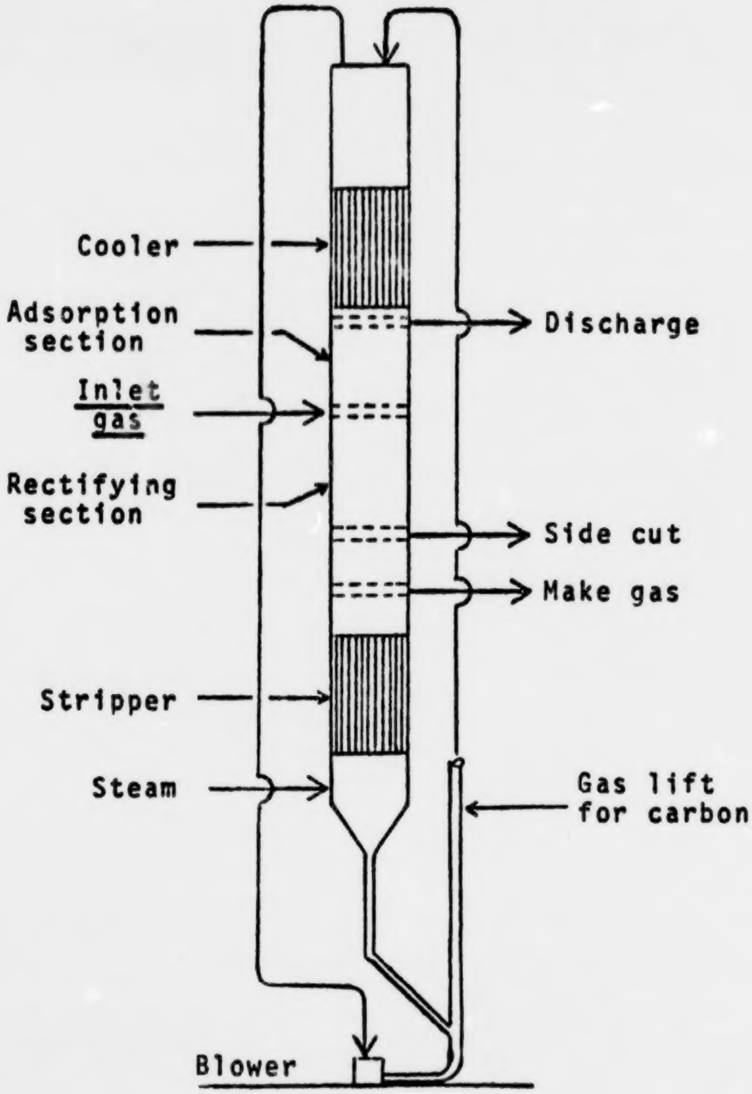


Figure 6-27 Moving-Bed System for Separation of Low Molecular-Weight Gases (Berg, 1947)

The disadvantages relative to other carbon-resorb systems are the higher structural costs and the loss of carbon by attrition because of movement through the column and the gas lift.

This system was described because the basic concept is a potential means for removal of low molecular-weight pollutants from air.

Rotating Axial-Flow Bed with Vapor Recycle

This system, proposed by Carr, MSA Research Corp., utilizes a rotating axial-flow carbon bed combined with a condenser and recycle scheme for recovery of the desorbed vapors. The carbon bed, illustrated in Figure 6-28, consists of a horizontal, segmented bed which is relatively shallow and rotates at about one revolution per hour or slower. The pollutant vapor recycle is accomplished by a purge airstream, which is circulated within the unit by a small blower. This recycle is illustrated in Figure 6-30. The main pollutant airstream is drawn down through the carbon bed and exhausted through the center duct by a blower located on the top of the unit. Part of the purified air forms the purge stream (regenerating gas) which is first drawn up through the cooling section of the carbon bed in order to cool the carbon and heat the purge stream. The purge stream is further heated by an electric heater and forced up through the regeneration section. The purge airstream, now loaded with the desorbed pollutant vapor, is cooled by heat exchange with the exhaust air and further cooled to a lower temperature in a small refrigeration unit where the contaminant is condensed and stored as a liquid. The purge airstream from the refrigeration unit is warmed by heat exchange with the purge air to the refrigeration unit and recycled by the blower above the carbon bed.

The rotation of the bed may be intermittent, i.e., rotated a distance of one or more segments at a time and held for a predetermined time period or it may be rotated continuously. When rotated intermittently, the desorption rate varies over the time period in a manner similar to curve given in Figure 6-19. When regeneration is performed over two segments simultaneously but the bed rotated a distance of one segment at each time period, the desorption rate is considerably steadier than indicated in Figure 6-19. However, any variation in desorption rate is undesirable because of adverse effects on any of the subsequent pollutant vapor disposal schemes that might be used. In this respect continuous rotation has its advantages.

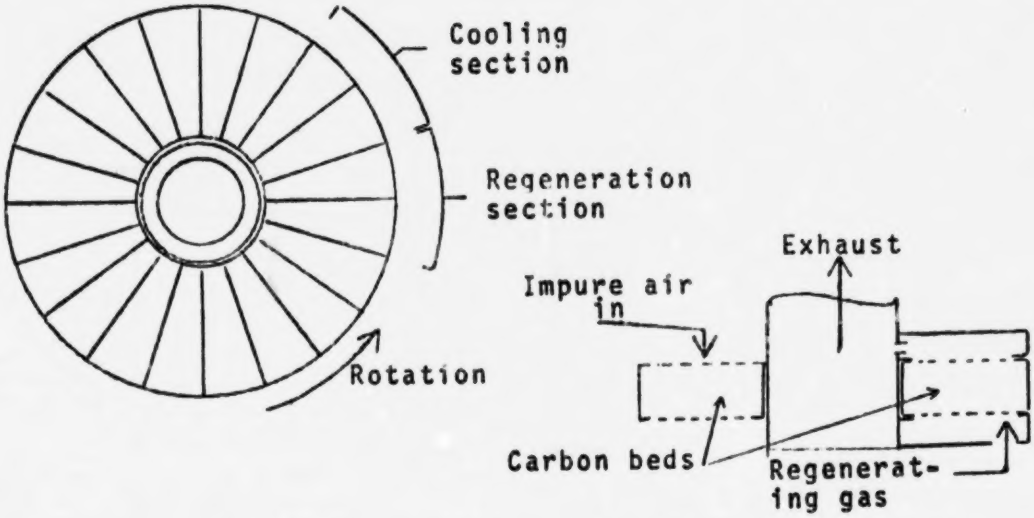
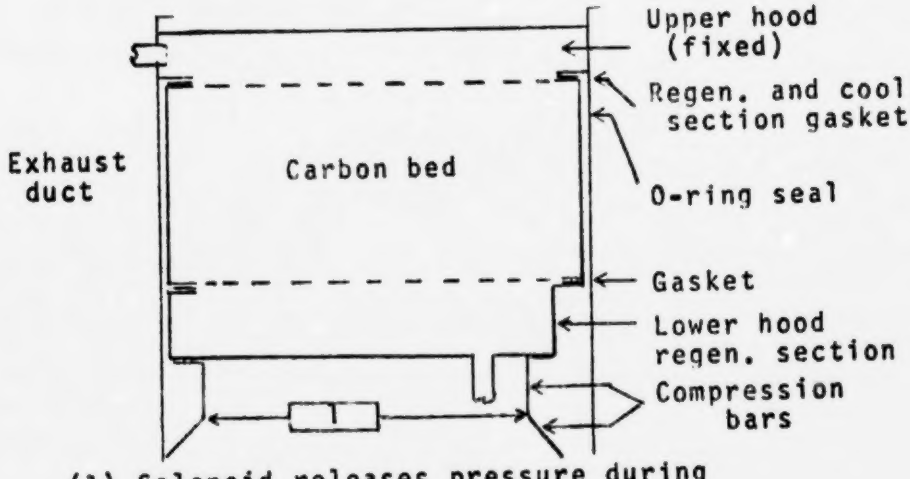


Figure 6-28 Rotating Axial-Flow Bed, Plan and Elevation



(1) Solenoid releases pressure during bed movement.

Figure 6-29 Rotating Axial-Flow Bed, Showing Seal Detail and Mechanism for Raising and Lowering Bed

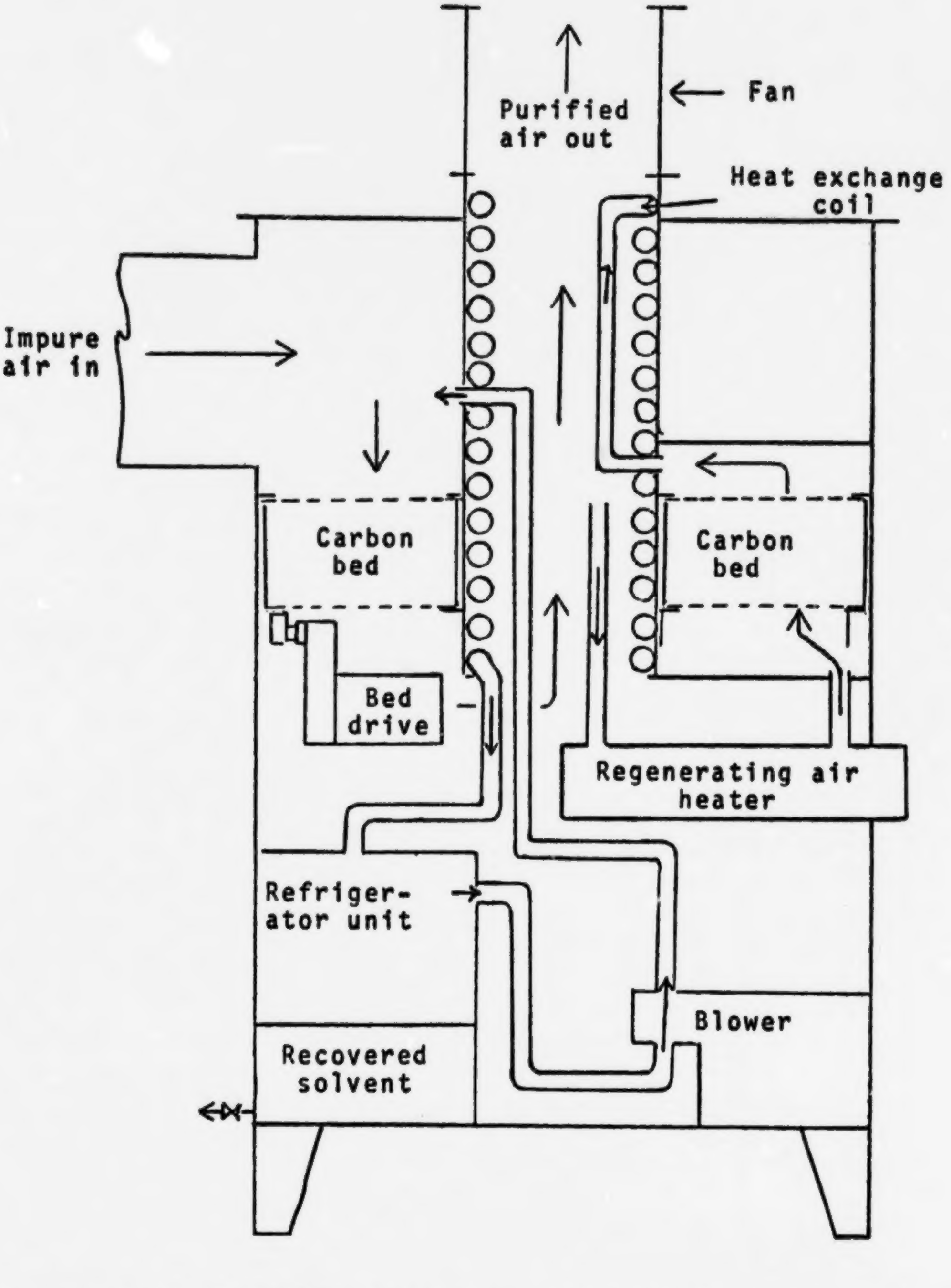


Figure 6-30 Rotating Axial-Flow Bed with Condenser and Recycle for Uncondensed Vapors, 3,800 ft^3/min Airflow Capacity, 6 ft Bed Diameter

The advantages of this system relative to the stationary bed, are compactness and efficiencies produced by continuous operation. The continuous discharge permits minimum size and utility requirements for the auxiliary recovery or disposal facilities. The disadvantages are those of maintaining seals, more elaborate and costly construction, and wear of moving parts. In regard to seals, continuous wear will occur when rotation is continuous. When rotation is intermittent, the bed can be lowered during rotation to lessen pressure against the seals and again raised to tighten the seals for the stationary time period. In this way maintenance on seals is lessened. Figure 6-29 illustrates the seal arrangement and mechanism for pressure release on the seals.

The effect of vapor recycle on the adsorptive capacity of the carbon is discussed in the previous text under Gas Regeneration with Condensation and Recycle.

Materials of Construction

As was the case for the air purification systems discussed in the prior text, one of the main concerns for carbon resorb systems is corrosion. Activated carbons in contact with a metallic surface establish galvanic cells when moisture or acidic vapors are present and thereby cause rapid oxidation at the contact interfaces. Many of the pollutants are directly corrosive to metals and some are decomposed during adsorption or regeneration forming corrosive acidic vapors. The latter can cause deterioration, not only of the retainer holding the carbon, but also of structural surfaces although the most rapid deterioration would be at the metal-carbon interface. To slow down or prevent corrosion, structural members subject to corrosion are constructed of stainless steel or Hastaloy, or if constructed of mild steel, are coated with corrosion resistant plastics. The surface coatings must also be resistant to elevated temperatures required during regeneration. When the carbon is continuously or intermittently moved through the bed, stainless steel construction is recommended since carbon is quite abrasive and would rapidly wear away any coatings that might be applied.

Auxiliary Equipment

The emphasis in the prior discussions of air purification and carbon resorb systems has centered on the adsorbent bed proper since it is the characterizing component of the overall system. Important to the effective functioning of the adsorbent bed and ultimate disposal of the pollutants are the other components of the overall system. The other components, listed in Table 6-IV, are considered auxiliaries to the functioning of the adsorbent bed although they may also be considered as integral parts of the overall system depending on one's point of view. It is, however, outside the scope of this manual to describe the auxiliaries in any detail but within the scope to describe their tasks or functions.

Table 6-IV Auxiliary Equipment for Sorbent Type Air Pollution Control Systems

Hoods and ducts
Filters and scrubbers
Air coolers
Blowers
Steam generators
Inert-gas heaters
Condensers
Refrigerating units
Decanters
Thermal incinerators
Distillation columns
Heat exchangers
Carbon reactivators
Monitors
Controls

Hoods and Ducts - Hoods to collect the pollutant vapors from the point sources with minimum airflow and ducting the collected vapors to the sorbent system are an economic necessity. By ducting, the quantity of air to be purified is kept smaller and the pollutant concentration maintained higher. Both act to reduce the size of the sorbent system required and to reduce the operating costs.

In existing operations, the retrofitting of ducts and the sorbent system can be a problem. Industrial processes are often designed to conserve space with little room remaining for later installation of pollution control equipment. Carbon resorb systems are frequently installed outdoors necessitating extra long ducts.

Filters and Scrubbers - When particulate matter is present in the pollutant airstream, it should be removed from the airstream prior to the removal of the vapors. Particulates tend to form coatings on surfaces they contact. When the particulate deposition occurs in air coolers and blowers their operating efficiencies decrease and cleaning becomes necessary.

Particulates plug adsorbent beds and thereby necessitate a costly replacement of the bed. Some particulate matters are toxic and should be completely removed for this reason.

Particulates may be removed from the airstream with large area fabric filters made of organic and/or glass fibers. These may be in a pleated form or bags. Bag filters have a beneficial feature in that they may be cleaned and used repeatedly.

Fabric filters of several efficiencies are available. The high efficiency filter is used when finely divided toxic material is present such as chemical warfare aerosols, bacteria or radioactive dust. These filters have an efficiency of 99.97% in the capture of 0.3 micron diameter particles. When the concern is more with protection of the adsorbent bed, an intermediate or roughing filter may be used. The intermediate filters are considerably less efficient than the high efficiency filters and are generally rated according to the National Bureau of Standards (NBS) atmospheric air stain test at over 30% efficiency. The roughing filter takes out the coarsest dust and are not rated according to NBS test. The cost and resistance to airflow increase as the efficiency is raised. As the filter becomes coated with particulates, its efficiency improves as also the resistance to flow. The initial resistance of the intermediate filters is between 0.25 to 0.55 in. of water pressure drop and when it rises to 1.0 in. during usage the filter is replaced.

Water scrubbers may under certain conditions be more effective than a dry filter. This is the case when the pollutant mixture contains highly soluble but poorly adsorbed vapors. When a scrubber is used a demister should also be used and the airstream heated to lower the relative humidity.

Air Coolers - Exhaust air or gases from industrial operations are generally at elevated temperatures. To maintain the adsorptive capacity of the carbon at an effective level and also to attain more uniform adsorption-regeneration cycles, the exhaust air is cooled down to at least 95°F.

Blowers - One or more blowers are required in the carbon resorb systems as described in the previous text of this chapter. For the main airflow stream the blower must overcome the resistance primarily of the carbon bed which can vary from 2 to 18 in. of water pressure drop. Additional resistance comes from the particulate filter which can vary from virtually zero to 1.0 in. of water. Resistances to flow in the ducts, valves and air cooler are small relative to the carbon bed resistance.

Figure 6-8 presents graphs giving the pressure drop through granular carbon beds of varied mesh size fractions and as function of flow velocity.

Additional, but smaller, blowers are required for gas regeneration, recycle of uncondensed vapors and circulation to secondary adsorber as described in the various proposed systems. In some cases the blower is operated at an elevated temperature near 300°F.

For the air purification systems, the total resistance to airflow can vary from less than 0.5 in. of water when a filter is used for nontoxic vapors, to over 1.5 in. of water, when a filter is required for toxic chemicals.

The power consumption to operate the blower is one of the operating costs and varies with air volume to be moved and resistance to flow.

Steam Generators - Unless steam is available from other operations in the plant, a steam generator is required for the carbon regeneration phase. A low pressure steam at near 212°F temperature has been found most effective in solvent recovery operations. Super heated steam has not been found to be much more effective than 212°F saturated steam. The enthalpy of the vapor at temperatures above 212°F vaporizes the condensed steam and thereby the latent heat of condensation is lost to the regeneration process. High temperature, high pressure steam could reduce the steam-to-solvent ratio but the benefit is offset by the initial cost of heavier constructed adsorber and valves.

Steam generation is one of the higher operating costs in solvent recovery operations.

Inert Gas Heaters - When steam regeneration is not feasible, the carbon bed can be regenerated with air heated indirectly by an electric or gas heater or the flue gas or products of combustion from the gas burner can be used directly as an inert gas. With inert gases, regeneration temperatures of 200° to 300°F can be safely used. Higher temperatures begin to have drawbacks in that cost savings are nil and decomposition of the adsorbed vapors are accelerated.

Heating of the regenerating gas is another operating cost but has been found to be small and does not appreciably affect the air purification cost.

Condensers - When steam regeneration is used in solvent recovery, a water cooled surface condenser is usually used to condense the steam and desorbed solvent vapors. The cooling water is one of the operating costs; the usual ratio of cooling water weight to condensed steam weight is 30 to 1.0.

In the system utilizing gas regeneration and vapor recycle, a condenser is used to liquify the vapors from the regenerating gas. Where lower than ambient temperatures are required this condenser would be cooled with a refrigerant.

Refrigerating Unit - Required to cool condensers.

Decanters - A virtually complete separation of the condensed solvent and steam condensate can be effected by decantation when the solvent is insoluble in water. Examples of much used solvents of this type are toluene, xylene, octane and naphtha. Theoretically, the method is effective even at large steam-to-solvent ratios of over 30.

However, a large portion of solvents, or pollutants of concern, are soluble to varying degrees. Such commonly used solvents as 4-methyl-2-pentanone and trichloroethene are slightly soluble. The steam condensate phase will always contain a small concentration of the solvent and thereby be a source of water pollution. When the steam-to-solvent ratio is small (less than 6.0) the solvent loss is not significant costwise and the decantation method is effective. As the steam-to-solvent ratio increases, the loss of solvent in the steam condensate increases and, ultimately, a point is reached where other methods of recovery become more economical, such as condensation with recycle or recovery with a secondary adsorber; see prior text on carbon resorb system. Often two phases are obtained, one rich in solvent and the other poor in solvent. This usually poses a disposal problem. In some cases the solvent rich phase can be distilled to recover the solvent and thereby defray the cost of disposal of the solvent poor phase.

Distillation Columns - Solvents that are soluble in the steam condensate can be separated from the steam by direct fractionation of the steam-solvent vapor mixture. This procedure is economical only when the steam-to-solvent ratio is low and the solvent quite valuable. Liquid phases are also obtained from decantation, which can be economically distilled.

Thermal Incinerators - When the desorbed pollutant vapor cannot be effectively recovered by steam regeneration and decantation or distillation, a more economical approach is to regenerate with a noncondensable gas and burn the desorbed vapor immediately. For this purpose a small thermal incineration is well suited. The size of the incinerator can be less than one tenth of the size normally required to incinerate the vapors from the primary airstream. See prior text under Gas Regeneration with Incineration.

Heat Exchangers - The proposed carbon resorb systems as illustrated by flow diagrams in Figures 6-17, -20 and -21 simultaneously heat and cool gas streams. By transferring the heat from one stream to another, savings on cooling water and fuel are realized.

Carbon Reactivators - In carbon resorb systems such as the multistage with bed displacement, Figure 6-25, and the fluidized bed, Figure 6-16, the carbon is removed from the portion of the system where the adsorption phase is performed. When the carbon shows signs of activity loss it can be readily passed through a high temperature steam activator operating at temperatures over 1600°F. This is the standard procedure with the multistage system. For large installations where a small activator can be operated continuously the cost of reactivation would be greatly reduced.

Monitors and Controls - In solvent recovery operations, the solvent to be recovered is known and its concentration determined from solvent usage rate and exhaust airflow rate. The service time to be expected may be known from past experience with other similar installations or can be estimated by using the procedures as described in Chapter 4. It then becomes a matter of setting a time schedule for change of adsorbers for the adsorption and regeneration phases. This can be automatically controlled with a timer and mechanically operated valves.

Manometers, to measure the pressure drops across the filter and carbon bed, signal the need for change of filter and/or carbon bed when a pressure rise occurs.

A temperature recorder before the bed can be used to determine the efficiency of the air cooler, if one is being used, and a temperature recorder on the effluent side of the bed can be used to monitor the time of adsorption zone penetration. The approach of the adsorption zone to the effluent end of the bed is accompanied by a temperature rise in the effluent stream. This can be used as a signal to change adsorbers.

Steam input during regeneration should be metered to avoid under or over regeneration and also timed to fit the regeneration phase within the overall cycle.

The auxiliary equipment, the condensers, distillation columns, incinerators, etc. also need to be monitored and their operations controlled to integrate them into the overall operations.

When the carbon resorb system is involved in less well defined areas of pollution control, the monitoring and control functions are more involved and difficult. It is necessary to identify the components and determine their concentrations in the pollutant airstream. These analyses are required before a decision can be made regarding the type and size of control system best suited for the particular emission source. At low pollutant concentrations the adsorption zone temperature can be so slightly different from that of the rest of the bed that it is not a reliable indication of the adsorption zone position in the bed. In cases of this type, a gas analyzer is required to signal the adsorption zone penetration of the bed and thereby avoid an overrun.

Chapter 8 discusses instruments that are suitable for monitoring the adsorbent systems operations.

Operation of Carbon Resorb System

Operating Parameters - Unlike the air purification systems, the carbon resorb systems are subject to a much greater variety of conditions which demand modifications to the equipment and modes of operation in order to attain the most effective and economical service for any particular application. The prior text, Carbon Resorb Systems, describes various proposed and successfully used systems which show the variety of equipment modifications that are possible. This part of the chapter discusses the operating parameters which form the rationale for these modifications. The operating parameters that are controlling to varying degrees are:

- Pollutant type
- Pollutant concentration
- Carbon type
- Temperature
- Flow velocity
- Adsorption-regeneration cycle frequency
- Regenerating agents

Pollutant Type - In assessing the pollution control situation for an adsorbent system, the most important property of the pollutant that should be considered is its molar volume, designated by V_m in this handbook. V_m is used in the adsorption potential equation, Equation 4-44 to calculate A as used in the generalized adsorption isotherms, Figures 4-11 and -12. The equation is reproduced in a modified form,

$$A = [T/V_m] \log [C_o/C_i].$$

The adsorptive capacity decreases with increased A and A increases with decrease in V_m because of the inverse ratio and also because C_o increases with decreasing V_m. See Chapter 4, Potential Theory Equations, for further discussion. Appendix C-1 gives the V_m values for pollutants of interest in control of small emission sources.

If V_m is between 80 and 190 cm^{3}liq/mol, there generally are no real problems encountered in the adsorption and desorption phases of the cycles. Exceptions occur when the adsorbed vapor polymerizes and V_m thereby increases by a large amount.

Vapors with V_m greater than 190 cm^{3}liq/mol tend to be difficult to desorb by the commonly used method, steam at 212°F, or by a noncondensable gas at temperatures up to 300°F. If a carbon resorb system is used and vapors of this type are dominant in the pollutant mixture, high temperature steam reactivation (over 1600°F) becomes a necessary part of the operating procedure and also becomes a substantial operating cost. The multistage system (Melshimer system) is designed for these conditions in that the transfer of carbon bed between the reactivator and adsorber can be done rapidly and with minimum of labor. The continuous-moving bed (Hypersorber) and fluidized bed systems are also readily adaptable to outside reactivation.

When the pollutant V_m are less than 80 cm^{3}liq/mol, each pollutant has to be evaluated separately because the effect of the functional group becomes pronounced, but the general trend is for these pollutants to be poorly adsorbed. The alternatives are to; (1) operate with a system that can be economically regenerated frequently or continuously, or (2) use an impregnated adsorbent that is specific for the pollutant.

Many pollutants have no recovery value. This creates a disposal problem after the pollutant has been desorbed from the carbon and alters the mode of operation, which may be different than used in solvent recovery. When the pollutant is completely combustible it can frequently be disposed of with the least cost by immediate incineration after desorption. When the pollution is noncombustible or contains groups or elements such as NO_x, SO_x or Cl that will repollute the atmosphere on incineration, it again becomes necessary to recover the pollutant and hold it in storage until some other means is used for its disposal.

Pollutants, or solvents, vary in their stability when in contact with the carbon, and the presence or lack of stability can considerably alter the operation and economics of the control system. For example, cyclohexane and trichloroethene are quite stable and carbon beds used in their recovery last over 10 years before replacements are necessary. 4-Methyl-2-pentanone undergoes a small amount of polymerization causing a shortening of useful bed life to 3 to 5 yr. 1,1,1-Trichloroethane decomposes forming an acid as one of the decomposition products. To avoid corrosion when recovering this solvent, Hastaloy construction is used. 2-Nitropropane decomposes yielding NO_2; carbon-bed fires have been reported when this solvent has been adsorbed. 2-Butanone decomposes to a small extent and carbon bed fires have also been reported in this case.

In any new situation, it is necessary to know the adsorbabilities of the pollutants and also their stabilities before the best suited control unit can be designed and its operating procedures worked out.

Pollutant Concentration - It is desirable to have the pollutant, or solvent, vapor concentration high, i.e., up to the 25% LEL, since the adsorptive capacity increases with concentration. A smaller carbon bed is then required to control the vapors emitted from any given source. The higher concentration allows operation with a larger operating capacity for a given regenerating agent usage. Equation 4-44 shows the effect of change in C_i on A and thereby on the adsorptive capacity.

The use of hoods, covering the point sources, and ducting of the pollutant vapors to the control unit, as a means for attaining higher concentrations, are important first considerations in assessing the pollution control situation. When the circumstances are such that the concentration is low and cannot be raised by such means, the other components of the system need to be designed so that the air can be purified as economically as possible. This may mean the use of an inert, noncondensable gas for regeneration rather than steam. The desorbed vapors may then be incinerated, or if incineration is not feasible, the desorbed vapors may be readsorbed in a secondary adsorber and recovered for later disposal as a liquid. The desorbed vapors may also be recovered by the condensation-recycle procedure as described earlier in this chapter under Gas Regeneration with Condensation and Recycle.

The heat evolved during adsorption can under conditions of high concentration create problems that lower the effectiveness of the carbon resorb system. The heat is evolved in the adsorption zone and most of the heat is initially absorbed by the carbon in the adsorption zone. The adsorption zone and heated-carbon zone move down the bed at the same rate. At high concentrations the temperature rise can be sufficient to lower the adsorptive capacity of the adsorption zone and thereby lower the bed capacity. The elevated temperatures can also cause vapor decomposition which may be especially undesirable in the presence of air. In such cases internal bed cooling is necessary as done by cooling coils. At low concentrations, the temperature rise is not sufficient to cause any problems. In solvent recovery operations, when temperature sensitive solvents are being recovered, the adsorbers are operated in such a manner that at least 12% moisture remains on the carbon after the steam regeneration. The desorption of the water during the adsorption phase moderates the temperature rise. See Chapter 4, Adsorption Thermodynamics, for discussion on heats of adsorption.

Carbon Types - Commercially available carbons offered for vapor phase adsorption by the manufacturers fall into fairly narrow ranges in regard to density and to adsorptive capacity as measured by the CCl_4 activity. The density range is 28 to 31 lb/ft^3 and CCl_4 activity range is 50% to 60%.

A variety of mesh sizes are available but those of greatest interest in carbon resorb systems utilizing fixed beds are the coarsest ranges, 4 to 6 and 4 to 10 U.S. sieve size. The coarsest mesh sizes are used to keep the resistance to airflow low although the coarse mesh size also lengthens the adsorption zone length. The economics favor the reduced pressure drop in this mesh size range. Carbons coarser than 4 to 6 become more expensive to manufacture, are more difficult to activate uniformly, are more friable and also produce a considerable increase in the adsorption zone length.

To know the response of a carbon under the many varied applications, a generalized adsorption isotherm for the carbon is necessary. This information is seldom offered as part of the sales literature. The CCl_4 activity gives the adsorptive capacity at only one point ($A = 2.5$) and is at near saturation capacity. The slope of the generalized adsorption isotherm (Figures 4-11, and -12) at A greater than 2.5 has a bearing on whether the carbon is best suited for solvent recovery or air pollution control at low vapor concentrations and for poorly adsorbed vapors. The isotherm with the steep slope and high CCl_4 activity is the better carbon for solvent recovery while the carbon with a small slope is better suited for adsorption at the low concentrations.

At times the ash content and ignition temperature of the carbon become important parameters. The type of ash present can affect the ignition temperature and can catalyze the decomposition of the adsorbed vapors.

Hardness becomes an important parameter in applications where the carbon is moved frequently as in the multistage, continuous moving bed or fluidized bed systems. In this respect the pelletized carbons show a greater resistance.

Additional information on carbons is presented at the end of this chapter under Adsorbents and Adsorbent Systems Manufacturers and Venders.

Temperature - Relatively small differences in the carbon bed temperature cause large differences in the adsorptive capacity. This is an important factor in regard to the adsorption and regeneration phases of the control process. The adsorption phase is carried out at as low a temperature as is practical and the regeneration at an elevated temperature at such a level where minimum damage is done to the carbon, the adsorbed vapor and equipment.

The temperature effect can be demonstrated in an approximate manner by use of Equation 4-44 and a generalized adsorption isotherm for any selected pollutant vapor. Table 6-V presents estimates on the effect of temperature on the adsorptive capacity for 4-methyl-2-pentanone on BPL V-type carbon, isotherms in Figure 4-12.

Table 6-V Effect of Temperature on Adsorptive Capacity and Equilibrium Concentration for 4-Methyl-2-pentanone Adsorbed on BPL V-Type Carbon

Temp., °F	ω, lb/lb when C_i=100 ppm	C_i, ppm when ω=0.20 lb/lb
77	0.20	100
105	0.17	300
120	0.15	640
212	0.07	13,000
300	0.03	110,000

As is apparent from the capacity figures in the second column, the capacity decreases with increased temperature. A temperature is ultimately reached where it is more economical to cool the airstream than to operate at the reduced capacity. The generally accepted upper temperature limit for the adsorption phase is near 120°F. At this temperature the capacity is already down to 75% of the capacity at 77°F. Some solvent recovery systems are operated at 105°F.

To regenerate the carbon, it is heated with steam or a noncondensable gas which also serve to sweep out the released vapors. Referring to Table 6-V, if the carbon bed, saturated to ω = 0.20 lb/lb, were sealed off and heated to 212°F the 4-methyl-2-pentanone concentration would rise to approximately 13,000 ppm and at 300°F to 110,000 ppm. On releasing the pressure a considerable amount of the vapor would desorb and with a sweep gas the desorption rate would be accelerated. To remove all of the adsorbed vapor, it would, however, require a large amount of sweep gas. At 212°F, when ω = 0.07 lb/lb and C = 100 ppm, the desorption rate would be very slow at practical sweep gas flow velocities. It is more economical to desorb only a part of the total capacity and limit the cycle to an "operating capacity".

Flow Velocity - When the total airflow from the pollutant emission source has been determined, the first step in sizing the carbon bed is the determination of the bed area that will give a practical flow velocity. The decision on the practical flow velocity takes into consideration the adsorption-regeneration cycle frequency, the bed dimensions and resistance to flow. For a given flow rate and concentration, the adsorption-regeneration cycle frequency is determined by the bed volume, or weight, and operating capacity. In solvent recovery the cycle time is near 1.0 hr while in pollution control the adsorption phase may last the duration of an 8-hr work day and the regeneration performed during off-working hours. The dimensions of the bed may now be adjusted for the fixed bed volume that will give the best compromise on the resistance to flow and the structural design of the bed. A bed with a large area and short length will operate at lower flow resistances but for structural reasons may not be the best design.

The air velocities commonly used are in the range 30 to 110 ft/min in the various types of carbon resorb systems. The trend is toward the higher velocities, particularly in the stationary bed solvent recovery systems. Bed lengths range from 8 to 36 in. In order to hold the flow resistance as low as possible, coarse, 4 to 6 mesh size, pelletized carbons are frequently used. High flow resistance, aside from consuming more power for the blowers, also cause operational problems with the valves.

When pressure drop measurements are not available for the particular carbon being considered, an estimated pressure drop can be read-off from predetermined curves such as shown in Figure 6-8, or calculated with Equation 4-42.

Flow velocity also affects the adsorption zone length, although in carbon resorb systems this is not a critical factor. Even at the 110 ft/min flow velocity and for coarse mesh carbons, the adsorption zone length is less than 4.0 in., compared to total bed length of 12 in. and longer. Equation 4-32 gives the relationship between flow velocity and adsorption zone length.

Adsorption-Regeneration Cycle Frequency - The optimum cycle frequency is attained when the combined cost of the adsorption and regeneration phases is at a minimum. For a fixed operating capacity, the adsorption phase cost increases with service time because of the cost of additional carbon required and the increase in the per unit-time power consumption for the blower. When the service time is shortened, i.e., regeneration frequency is increased, the regeneration cost rises because of the additional fuel consumption for the more frequent heat-up of the carbon bed and associated hardware. Steam utilization is also less efficient for the shorter carbon bed. The adsorption phase time period and the regeneration phase time period need not be equal although equal phase time periods have worked-out best for stationary bed solvent recovery systems.

To avoid underrun or overrun on the adsorption or regeneration phases, monitoring devices are desirable to signal the completion of each phase. For the adsorption phase, the monitoring device would be required to detect the penetration of the adsorption zone lead edge. For the regeneration phase, the monitoring device would be required to measure the vapor concentration in the regenerating agent and, when the concentration has dropped to a predetermined level, signal the end of the regeneration phase.

Regenerating Agents - The regenerating agent used in solvent recovery is steam. It has several properties that make it uniquely suited for this purpose. Its saturated vapor temperature is at a temperature level where many of the solvents of recovery value are poorly adsorbed or become readily desorbable, but the temperature is not too high to cause extensive damage to the solvents. The heat of condensation is high, hence saturated steam rapidly delivers a large amount of heat to the carbon at virtually a constant and moderate temperature. A great many solvents are fairly insoluble in water; condensation of the steam-vapor mixture and decantation effect a satisfactory separation and liquid solvent recovery. Steam is fairly inactive with most solvents although some decomposition is reported either because of direct action with the steam and/or catalytic help from the carbon. The steam also provides an atmosphere in which combustible vapors can be handled safely at high concentrations.

In solvent recovery with steam regeneration the carbon acts as a collector or transfer medium. It collects the solvent from the noncondensable air and transfers it to the condensable steam from which it can be readily separated by decantation or distillation. Usually the volume of steam used is not much less than the vapor-laden air and the concentration of solvent initially in the airstream is not much less than the solvent concentration in the steam.

In air pollution control applications where the pollutant concentrations are low and, in addition, the pollutants may have no recovery value, steam regeneration is frequently not the best regenerating agent. Because of the adsorption at low concentrations, the vapors are held tightly by the carbon and, relative to the amount of pollutant adsorbed, the amount of steam required is large. Under these conditions even slightly soluble organic compounds are completely dissolved in the steam condensate. Under these circumstances the more economical approach is to regenerate with a noncondensable gas such as air, or, if there is danger of explosion, regenerate with an inert noncondensable gas such as flue gas. As already described earlier in this chapter the use of noncondensable gas entails considerable changes in equipment and operating procedures.

In the adsorption processes at the low pollutant concentration, the carbon acts as a concentrator. The carbon collects the pollutant vapor from a large volume of air over a long period of time during the adsorption phase. During regeneration the vapors are released from the carbon at a high concentration, in a relatively small volume of regenerating gas, and in a relatively short period of time. Disposal of the pollutant now becomes an easier task. The effluent mixture of regenerating gas and pollutant vapor may now be treated in a small incinerator to burn the vapor, or be passed through a condenser to liquify the vapor for separation, or readsorbed in a secondary adsorber and recovered by steam regeneration.

Polar Adsorbent Systems

No installations appear to be in service for air-pollution control which utilize the polar adsorbents: silica gel, activated alumina or molecular sieves. They are, however, being investigated for this application under very specific conditions. The molecular sieves have a potential application for control of SO_x and NO_x from exhaust gases. Because of the polarity and water solubility of these molecules, they can be effectively adsorbed from a humid airstream. Silica gel and activated alumina have a potential application in the control of high molecular weight vapors (of V_m greater than 190 cm^3/mol) from dry airstreams. Their greatest usefulness is as desiccants and also for the separation of dry organic liquids and vapors. See Chapter 4, Adsorbent Types, for discussion of polar adsorbents.

For air pollution control the systems design would not be greatly different from the carbon resorb type. Some modification would be required because of differences in mode of regeneration. Steam or water would be the most probable regenerating agent. Prior to start of the adsorption phase, the water would have to be removed from the adsorbent. Molecular sieves require fairly high drying temperatures.

Impregnated Adsorbent Systems

Iodine impregnated carbons are used in atomic energy plants to prevent escape of radioactive methyl iodide in case of a breakdown of the reactor. This is an exchange reaction of radioactive iodine in the methyl iodide with nonactive impregnant on the carbon. The type filter used is illustrated in Figures 6-3 and -4. These are considered nonregenerative although in time the radioactivity would decay completely.

For toxic chemicals such as phosgene, cyanogen chloride and hydrogen cyanide, carbon impregnated with copper oxide and hexavalent chromium are very effective. The type filter used is illustrated in Figure 6-3. These are nonregenerative. When the chemicals have reacted with the stoichiometric amount of pollutant, the carbon is replaced.

Catalyst Impregnated Carbon Systems

The use of catalytic impregnants to permit in-place reactivation of a spent carbon bed was proposed and laboratory tested by Turk (1955). The carbon is impregnated with 2% to 3% of an oxide of chromium, molybdenum, tungsten, cobalt or copper. After the carbon has become saturated with organic vapors by normal adsorption, the reactivation is initiated by raising the temperature of the bed to effect catalytic oxidation of the adsorbed organic compounds or their vapors as they are being desorbed.

As in catalytic incineration, the oxidation rate increases with increased temperature, i.e., complete oxidation becomes more probable as the temperature is raised. In catalytic incineration, operating temperatures at which combustion efficiencies are 90% and better with reasonable sized units are in the range 600° to 900°F. Ignition temperatures of carbons vary but are between 600° to 700°F, hence the optimum temperatures for combustion catalysis cannot be used. Some sacrifice in regard to completeness of combustion is necessary unless some corrective measures are taken. A corrective measure that can be taken to avoid air pollution by the combustion products is to recycle the gases through the bed or install a small thermal incinerator to complete the combustion. Discussions on catalytic incineration are given in Chapter 7 and on the use of thermal incinerators for combustion of desorbed pollutants are given in this chapter under Carbon Resorb Systems.

The potential advantage over an unimpregnated carbon system would occur when the pollutants are of type that polymerizes on adsorption, thus making their desorption impossible by the more conventional regeneration procedures, or are nondesorbable because of high molecular weights. In-place catalytic oxidation of these pollutants to lower molecular weight components would effect their desorption.

The construction of the adsorbent system would be similar to those already described for carbon resorb but modified so that regeneration at temperatures up to 600°F are possible.

Economic Analyses

General Discussion

In the evaluation of the adsorbent systems relative to the catalylic and thermal incineration systems, the final decision as to which type of system should be used for a given control problem is based on the cost of cleaning a unit volume of air. When a cost analysis clearly indicates that a carbon resorb system should be used, further analysis involving the operating parameters can indicate the optimum operating procedure. An approach is taken in this section of the chapter that supplied answers in both of these areas.

To work up the estimated costs of air pollution control, data on various operating costs are required. Common to all three types of systems are the costs of:

Depreciation
Operating labor
Maintenance
Electric power
Fuel

The catalysts used in catalytic incinerators frequently deteriorate faster than the rest of the system. Its replacement thereby becomes a direct major operating cost and should be added to the above list when referring to catalytic incineration. Frequently, activated carbons also deteriorate faster than the rest of the system; the replacement cost should be added to the above list when referring to carbon resorb systems. An additional cost in the operation of some carbon resorb systems is that of cooling water used for vapor condensation. In order to determine the depreciation cost, the initial equipment and installation costs (fixed capital) should be ascertained.

Cost estimates for carbon resorb systems were prepared for 4-methyl-2-pentanone, trichloroethene, and propanone at influent flow concentrations of 10, 100, 300, 500, 1000 and 3000 ppm and flow rates of 800 and 3,800 ft³/min. The estimates are presented on a $/hr per 1000 ft³/min flow rate basis. The systems analyzed are:

1. Stationary bed with steam regeneration and solvent separation by decantation
2. Stationary bed with air regeneration and thermal incineration of combustible desorbed pollutant vapors
3. Rotating axial flow bed with air regeneration, desorbed vapor condensation and vapor recycle.

Comparative costs of air cleaning at varied pollutant concentrations are presented for carbon resorb and the incineration systems. The effect of pollutant molar volume, pollutant concentration, flow rate, and adsorption-regeneration time on the cost of air cleaning are also investigated.

Operating Costs

Fixed Capital - Cost information for the catalytic and thermal incineration processes was collected from several sources: ASHRAE (1966 and 1967), Meinhold (1963), UOP, and Phillip (1971). Equipment and/or depreciation costs from these sources were generally for larger capacity systems than the 3,800 ft³/min airflow. In these cases the 0.6 power factor was used to estimate the cost for the system at the 3,800 ft³/min flow capacity, thus:

$$\text{Cost for 3,800 system} = [3{,}800/F]^{0.6}[\text{cost of larger system}]$$

where F is the flow capacity of the larger system.

Installed costs for the catalytic incinerator vary between $3,500 and $6,000 per 1,000 ft³/min air handling capacity. The higher end of the range includes cost for heat exchangers, filters for particulate removal and also reflects the costs of more expensive catalysts. As the size increases, the cost per 1000 ft³/min flow capacity decreases to some extent, but for the range 2,000 to 10,000 ft³/min flow capacities, the costs per unit flow volume were assumed essentially constant. For these estimates, the higher \$6,000 figure was used at concentrations below the self-sustaining concentrations (below about 3,000 ppm), since heat exchangers give a decided operating cost reduction. For the 3,800 ft³/min system the installed cost is then \$23,000.

The installed cost for a thermal incinerator of 3,800 ft³/min airflow capacity, with heat exchanger is approximately \$29,000 or \$7,600 per 1,000 ft³/min capacity.

For custom designed solvent recovery systems, the installed cost will usually range from \$10,000 to \$15,000 per 1000 ft³/min airflow capacity. Package type systems are available at a considerably lower cost. The equipment cost at the manufacturer's plant can range from \$2,000 to \$3,500 per 1,000 ft³/min capacity. Freight and installation costs must be added to these figures (Cooper, 1967).

For the air pollution control cost estimates presented here, the base prices on stationary bed systems are those provided by Vic Manufacturing Co. and Hoyt Manufacturing Corporation. Table 6-VI presents the approximate systems costs and sizes over a range of airflow capacities from 700 to 5,000 ft³/min per adsorber. Single and double adsorber systems of 3,800 ft³/min capacity cost \$19,480 and \$32,500, respectively. Installation costs raise the fixed capital costs to \$21,500 and \$35,800, respectively. A cost estimate was also prepared for airflow of 800 ft³/min. A dual adsorber system at this capacity level costs \$6,200 and when installed, \$7,000.

For the stationary bed utilizing air regeneration and thermal incineration, the above costs were used for the adsorber section of the system and cost added for scaled down sized thermal incinerators. The installed cost of a single adsorber, 3,800 ft³/min capacity system with desorbed vapor incinerator operating at regenerating gas flow range of 200 to 500 ft³/min is approximately \$26,000.

For the axial flow bed continuous recycle system, it was necessary to work-up the cost from basic component parts. The size and cost for a 3,800 ft³/min capacity system varies some with type of pollutant and concentration. The installed cost range is \$16,500 to \$19,800.

Depreciation - For the carbon resorb, catalytic and thermal incineration systems, a 10-year depreciation rate

Table 6-VI Packaged Vapor Adsorption and Recovery Systems, Approximate Equipment Cost and Size(1)

(1 Tank)(2) ft^3/min	Base price, $	No. of tanks	Auto. or manual	Motor HP	Carbon per tank lb	Shipping weight, lb	Size, in. w x l x h
700	1,280	1	M	3/4	350	1030	49 x 45 x 81
750	2,180	1	M	1	350	1100	49 x 45 x 81
750	3,340	2	M	1 1/2	350	1500	77 x 45 x 81
800	3,920	2	M	2	350	1650	77 x 45 x 81
800	4,070	1	A	3	350	1950	--
800	6,160	2	A	3	350	2400	63 x 84 x 95
1700	6,820	1	A	7 1/2	1000	4000	--
1700	5,280	1	M	7 1/2	1000	4000	--
1700	10,770	2	A	7 1/2	1000	7000	67 x 118 x 114
1700	8,080	2	M	7 1/2	1000	7000	--
3000	10,100	1	A	20	1500	4800	--
3000	16,540	2	A	20	1500	9300	92 x 97 x 137
3800	19,480	1	A	30	3000	12000	--
3800	32,500	2	A	30	3000	18000	111 x 182 x 140
5000	38,800	2	A	--	5400	--	--

(1) Based on information provided by: Hoyt Manufacturing Corporation and Vic Manufacturing Company.

(2) Tank or adsorber.

is used in the estimates prepared in this handbook although systems lives of up to 20 yr are claimed under various circumstances. The control system life can vary considerably, before major repairs are required, depending on corrosiveness of the pollutant vapors, frequency of the adsorption-regeneration cycles, and continuity of operation, i.e., whether intermittent or continuous.

For the estimates in this handbook, an 8-hr da, 2080-hr yr, operating basis was used. For carbon resorb systems, the depreciation cost on the 8-hr basis is approximately one-half of the total operating cost. For the incinerators, the depreciation cost on the 8-hr basis is about one-third of total cost at low concentrations but approaches one-half at 25% LEL concentrations. By adjusting the operating time closer to continuous operation, the total operating cost can be reduced by 30%. The estimated cost figures are on the high side in this respect but retain their correct relative positions for the three types of systems.

Operating Labor - Low labor costs are generally claimed for the operation of the carbon resorb and incineration systems. A low level of operating cost has been estimated on the basis of 5 min of labor per 8-hr shift for each 1,000 ft^3/min capacity (Hein, 1964). For the estimates for this handbook a considerably lower labor rate is used, $300/yr at $10 per man hour.

Maintenance - Yearly maintenance costs for catalytic incinerators have been estimated by some analysts on the basis of 10% of the initial incinerator cost (Hein, 1964). Other methods can consist of periodic catalyst replacement cost combined with a low percentage rate of the initial incinerator cost. For the estimates in this handbook, the overall yearly maintenance cost combines a $1,200/yr catalyst replacement cost and a 2% of initial capital.

For the thermal incineration a straight 2% of initial capital is used for the yearly maintenance cost.

For the carbon resorb systems, the overall yearly maintenance cost combines a $300/yr carbon replacement cost and a 1% of initial capital.

Electric Power - The main electrical power consumer is the air circulating blower. The kilowatts to move 1,000 ft^3/min of air through the incinerator or carbon resorb bed can vary from 1.5 to 6.0 depending on resistance to flow. Local electrical costs per kilowatt-hour will determine the power costs.

For the stationary bed carbon resorb systems, which are operated at bed lengths of 30 in., the blower power consumption is about 6 kilowatts per 1,000 ft^3/min. Additional but small power requirements are needed to operate monitoring and control devices. At a rate of $0.015/kwh, the yearly cost of electrical power for 2080 hr of blower operation is $710. An additional $60/yr for the other power costs brings the total to $770/yr. For the rotating axial flow bed system with condensation and vapor recycle, electric power is also required for refrigeration and regenerating gas heating. For the incinerators which operate at lower airflow resistances, the power cost is $500/yr.

Fuel - Fuel in the form of natural gas is required in steam and noncondensable gas regenerations, and to preheat the air-pollutant mixtures for the incineration processes. Natural gas costs vary for different locations but a generally accepted average cost figure is $0.60 per 1,000 ft^3 or $0.60 per 10^6 Btu. On the basis of gas consumption, steam generation costs $0.60/1000 lb, but due to heat losses, the generally accepted cost is $1.00/1000 lb. Noncondensable regenerating gas heating costs are considerably less than for steam because no latent heat is involved. To heat air to 300°F, the cost is about $0.05/1000 lb and to heat air to 400°F, $0.07/1000 lb. The amount and type of regenerating agent required varies with the influent concentration and pollutant type, see Chapter 4, Regeneration of Activated Carbons for further discussion.

Fuel costs to preheat the pollutant airstream for the incineration processes vary considerably with the concentration and to a lesser extent with type. Preheat requirements are discussed in Chapter 7, under Pollutant Concentration.

Cooling Water - Cooling water is required to condense the steam-pollutant vapor mixture. The ratio of cooling water at ambient temperature to steam is 30 to 1.0. Water cost varies with the locality but the generally accepted cost is $0.10/1000 gal. Cooling water may also be used for condensation of vapors from noncondensable regenerating gas.

Pollution Control Costs

Comparative Costs of Competing Systems - Relative pollution control costs for the competing systems are graphically presented in Figure 6-31. It is recognized that actual operating costs can vary markedly depending on local utility rates, operating time, choice of operating conditions, and sophistication or completeness of the system. The cost

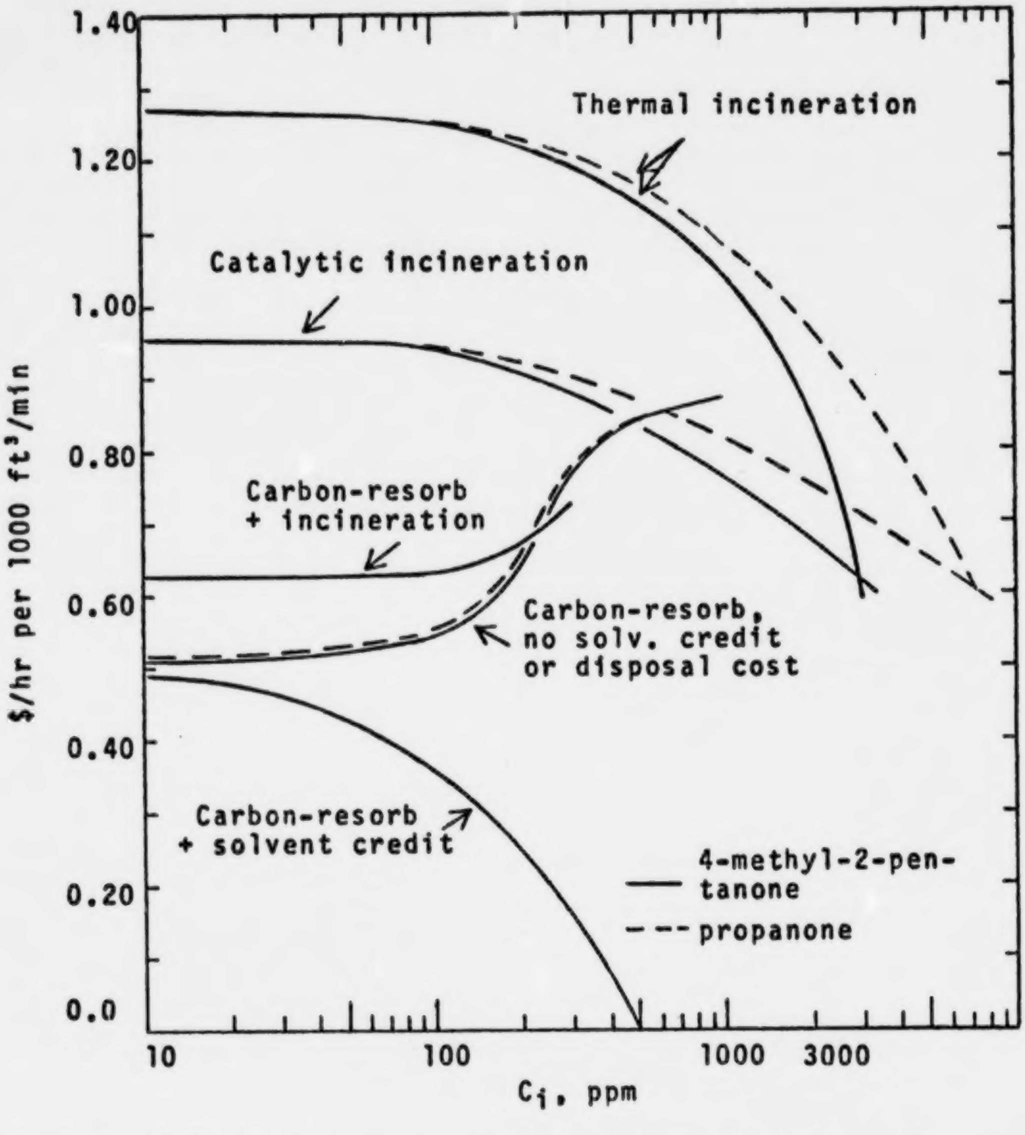


Figure 6-31 Comparative Costs of Pollution Control with Carbon Resorb, Catalytic Incineration and Thermal Incineration, 3,800 ft^3/min Capacity System, Calculations Based on 4-Methyl-2-pentanone and Propanone, 2080 hr/yr Operating Time.

factors that were used are detailed in Tables 6-VII and -VIII. In some cases, it may be possible to ratio the cost factors to reflect actual local conditions.

Minimum pollution control costs result where credit can be taken for the recovered solvent as indicated by the lowest curve in the figure (for 4-methyl-2-pentanone). Although this solvent is slightly soluble in water, it was assumed in making the solvent credit calculations that complete recovery had been effected (by decantation) even at operations at the 10 ppm influent concentration level. The curve illustrates the results achievable where solvent recovery is feasible and the solvent has recovery value. In this case the cost breakeven point is at C_i = 500 ppm; recovery operations at C_i greater than 500 ppm would be profitable. The breakeven point varies. For some solvents it is at C_i over 1,000 ppm, but a good average is at C_i = 700 ppm.

Below about 200 ppm and assigning neither credit nor disposal cost to the recovered solvent, the lowest pollution control cost is still indicated for the carbon resorb system. In this concentration range, a single adsorber unit operating on an eight-hour working cycle with regeneration at night was assumed. Here the cost level is just above $0.50. The sharp increase in operating cost, to over $0.80, shown between 200 and 500 ppm, results from the switch to a double adsorber unit, because of the necessary increase in frequency of regeneration. The cycle time here is one hour.

The next lowest operating cost, below 200 ppm, is shown for a combination of carbon resorb and thermal incineration. In this system the resorb unit is used to concentrate the pollutant to 25% of LEL before incineration. Air heated by the combustion unit exhaust is used for carbon regeneration. The pollution control cost is slightly over $0.60 but begins to rise rapidly at concentrations above 200 ppm because of the increase in cycle frequency and need for an increasingly larger back-up incinerator.

As shown by the upper two curves, catalytic and thermal incineration provide the lowest disposal costs at pollutant concentrations above about 1000 ppm.

Pollutant Molar Volume - The effect of pollutant molar volume on the air cleaning cost was investigated for the three vapors under study. The results are summarized in Table 6-IX. They show no significant differences although the V_m range brackets a considerable portion of the pollutants of interest. These cost figures are for steam regeneration with no credit for pollutant recovery or disposal cost, i.e.,

Table 6-VII Cost Factors for Air Pollution Control by Carbon Resorb Systems

Design basis

Airflow: 3800 ft³/min at 77°F
Pollutant: 4-methyl-2-pentanone
Carbon: 4 to 6 pelletized, 3000 lb/adsorber
Operation: 8 hr/da, 2080 hr/yr

	Typical resorb unit				Resorb + incineration		
Influent concentration, ppm	10	100	500	1000	10	100	300
Regenerating agent	Steam	Steam	Steam	Steam	Air	Air	Air
Regenerating agent temp., °F	212	212	212	212	200	200	200
Number of carbon adsorbers	1	1	2	2	1	1	1
Installed equipment cost, $	21,500	21,500	35,800	35,800	26,000	26,000	26,000
Airflow to incin., ft³/min	--	--	--	--	200	200	500
Operating costs, $/yr							
Steam at $1.00/1000 lb	208	400	800	900	--	--	--
Water at $0.10/1000 gal	80	154	310	350	--	--	--
Power at $0.015/kwh	770	770	770	770	800	800	800
Gas at $0.60/1000 ft³	--	--	--	--	610	610	1,420
Operating labor at $10/hr	300	300	300	300	300	300	300
Carbon replace (5-yr life)	300	300	600	600	300	300	300
Maintenance	215	215	360	360	390	390	390
Depreciation (10-yr life)	2,150	2,150	3,580	3,580	2,600	2,600	2,600
Total	4,023	4,289	6,720	6,860	5,000	5,000	5,810
$/hr per 1000 ft³/min	0.51	0.54	0.85	0.87	0.63	0.63	0.73
Pollutant recovered, lb/yr	1,090	10,900	54,500	121,000	--	--	--
Pollutant value at $0.135/lb, $/yr(1)	147	1,470	7,300	16,300	--	--	--
Operating cost - rec. value $/hr x 1000 ft³/min(1)	0.49	0.36	0	--	--	--	--

(1) Cost of separating pollutant from condensate not included.

Table 6-VIII Cost Factors for Air Pollution Control by Catalytic and Thermal Incinerators

Design basis

Airflow: 3800 ft³/min at 77°F
Pollutant: 4-methyl-2-pentanone
Operation: 8 hr/da, 2080 hr/yr

	Catalytic(1)				Thermal(1)			
Influeht conc., ppm	10	100	1000	3000	10	100	1000	3000
Installed equipment cost, $	23,000	23,000	23,000	23,000	29,000	29,000	29,000	29,000
Operating cost, $/yr								
Power at $0.015/kwh	500	500	500	500	500	500	500	500
Gas at $0.60/1000 ft³	2,900	2,750	1,400	200	5,800	5,600	3,960	320
Operating labor at $10/hr	300	300	300	300	300	300	300	300
Catalyst replacement	1,200	1,200	1,200	1,200	--	--	--	--
Maintenance, 2%	460	460	460	460	580	580	580	580
Depreciation, (10-yr life)	2,300	2,300	2,300	2,300	2,900	2,900	2,900	2,900
Total	7,660	7,510	6,160	4,960	10,080	9,880	8,240	4,600
$/hr x 1000 ft³/min	0.97	0.95	0.78	0.63	1.27	1.25	1.04	0.58

(1) 50% heat recovery

the pollutant and steam condensates are sewered. When recovery or disposal (by nonpolluting means) is carried out, the costs become variable depending on concentration, combustibility and water solubility.

Table 6-IX Effect of Pollutant Molar Volume and Concentration on Air Cleaning Cost When No Pollutant Recovery or Disposal Cost is Considered

	4-methyl-2-pentanone	trichloroethene	propanone
V_m, cm^{3}liq/mol	140	94	74
—— Costs when C_i = 3,000 ppm, \$/hr per 1,000 ft^3/min ——			
Steam and cooling water	0.23	0.21	0.23
Fixed	0.71	0.71	0.71
Total	0.94	0.92	0.94
—— Costs when C_i = 1,000 ppm, \$/hr per 1,000 ft^3/min ——			
Steam and cooling water	0.16	0.16	0.17
Fixed	0.71	0.71	0.71
Total	0.87	0.87	0.88
—— Costs when C_i = 100 ppm, \$/hr per 1,000 ft^3/min ——			
Steam and cooling water	0.07	0.07	0.08
Fixed	0.47	0.47	0.47
Total	0.54	0.54	0.55

Pollutant Concentration - The effect of pollutant concentration on air cleaning cost is shown in Figure 6-31 and Table 6-IX. The general pattern is for the air cleaning cost to rise with increased concentration. With reference to Table 6-VIII, the cost at C_i = 3,000 ppm is at the \$0.90 level while at C_i = 100 ppm it is at the \$0.50 level. When disposal of pollutant of no recovery value is added to the process, the costs rise but the cost pattern remains. Only when a pollutant of value is recovered is the pattern reversed, as shown by the lower curve in Figure 6-31.

Flow Rate - The effect of flow rate, or more correctly the flow capacity, on air cleaning cost does not follow the usual pattern observed, i.e., decreased cost with increased size. Cost figures worked up for Table 6-X show a small increase in air cleaning cost when a larger unit is used.

Table 6-X Cost Factors for Air Pollution Control by Carbon-Resorb Systems at Two Flow Capacities

Design basis

Pollutant: 4-methyl-2-pentanone
Concentration: 1000 ppm
Carbon: 4 to 6 pelletized, vapor phase
Operation: 8 hr/da, 2080 hr/yr

Flow rate	800 ft³/min	3,800 ft³/min
Installed equipment cost	$7,000	$35,800
Pounds carbon/adsorber	350	3,000

Operating costs, $/yr

Steam at $1.00/1000 lb	190	900
Water at $0.10/1000 gal	75	350
Power at $0.015 kwh	80	770
Operating labor at $10/hr	200	300
Carbon replacement (5-yr life)	70	600
Maintenance, 1.0% of invest.	70	360
Depreciation, (10-yr life)	700	3,580
Total	1,385	6,860
$/hr per 1,000 ft³/min	0.83	0.87

Two operating costs, the operating labor and maintenance, are subject to adjustment which could reverse the air cleaning cost figures. The general impression is that at least in the flow capacity range from 800 to 10,000 ft³/min the air cleaning costs do not vary greatly with size change.

Adsorption-Regeneration Cycle Time - Every air pollution operation can be optimized with respect to the adsorption-regeneration cycle time length. For a given control situation the cycle time is dependent on the operating capacity selected. Operating capacity is the difference between the saturation capacity, ω_s, at the particular influent concentration, C_i, and the mean amount of adsorbed pollutant, ω_r, remaining on the carbon after regeneration.

The primary cost factor that varies with the cycle time is the steam consumption, hence a study of steam consumption as function of cycle time or operating capacity leads directly to the cycle time effect on air cleaning cost. Results of this type calculation are presented graphically in Figure 6-32. For these calculations, the carbon resorb system consisted of two beds with 3,800 ft³/min airflow capacity for each bed. 4-Methyl-2-pentanone at 500 ppm concentration was used as the representative pollutant. As shown in the figure, the steam consumption for heating decreases as the cycle time increases. This reflects the decrease in number of times the carbon and associated hardware have to be heated. The steam consumption for sweeping the pollutant vapors out of the bed increases rapidly with increase in cycle time. This reflects the decrease in vapor pressure as the pollutant is progressively removed from the carbon. (See Chapter 4, Regeneration of Activated Carbon for further discussion.) For this particular system, the total steam consumption passes through a minimum at the 2-hr cycle time.

Table 6-XI gives the operating capacity, $\omega_s-\omega_r$, the number of cycles per year and the air cleaning cost ($/hr per 1,000 ft³/min) for the above discussed pollution control conditions when no credit for recovered vapor or vapor disposal cost is taken into consideration. The minimum cost is $0.83 at the 2-hr cycle time or 0.024 lb/lb operating capacity. Over the cycle time range investigated, the cost differences are not large, but the cost difference would become very large at cycle times over 5 hr. At concentrations larger than 500 ppm, the minimum cost shifts to cycle times approaching the 1-hr level and at smaller concentrations the minimum cost shifts to cycle times longer than the 2 hr.

Table 6-XI Effect of Cycle Time on Cost of Air Cleaning for 3,800 ft³/min Carbon-Resorb System, 500 ppm Pollutant Concentration with Steam Regeneration

Cycle time	1 hr	2 hr	5 hr
$\omega_s-\omega_r$, lb/lb	0.012	0.024	0.061
Cycles/yr	2080	1040	416
$/hr per 1000 ft³/min	0.85	0.83	0.89

Rotating Bed with Condensation and Recycle - To determine whether some of the proposed innovations to the more conventional single or double stationary bed solvent recovery systems can be more economical for air pollution control, cost

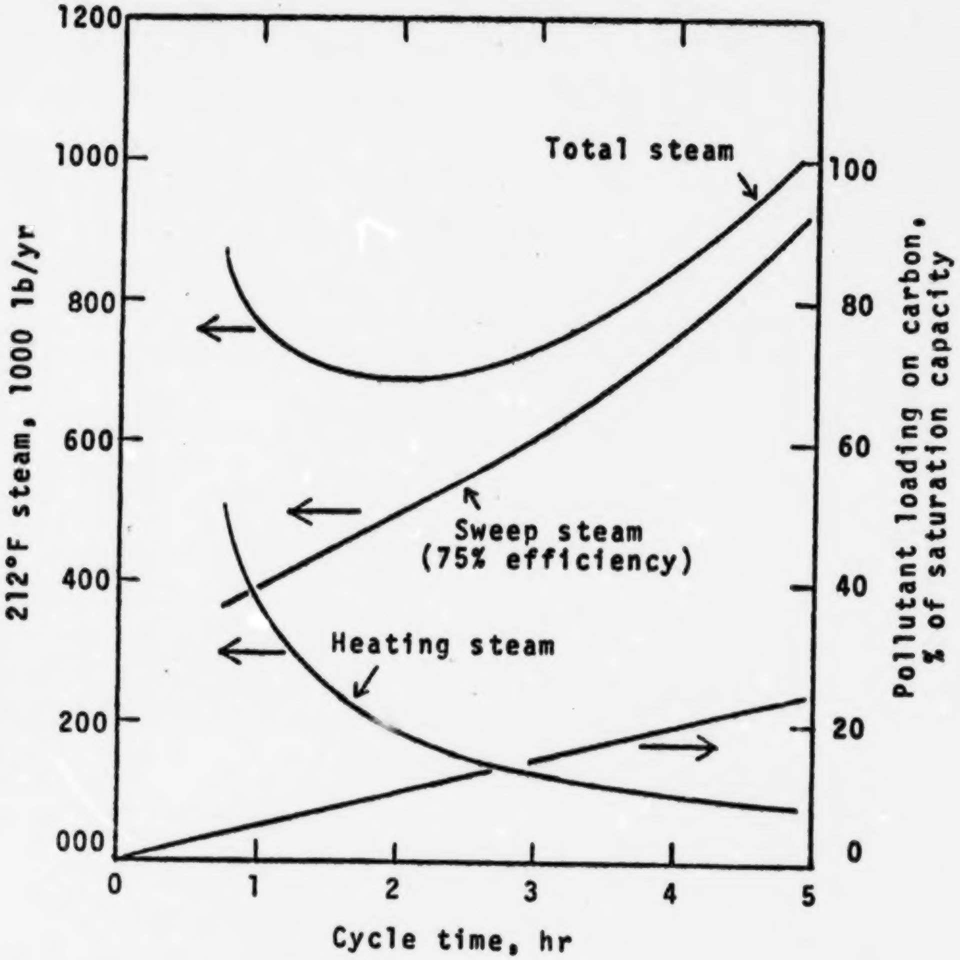


Figure 6-32 Steam Requirement for Regeneration vs Pollutant Loading and Cycle Time, Carbon-Resorb System on 4-Methyl-2-pentanone, 3,800 ft³/min Flow, 2080 hr/yr Operating Time.

estimates were worked up for the continuous vapor recycle system. This system utilizes hot air regeneration, recovery of desorbed vapors by condensation and recycle of unadsorbed vapors to the carbon bed. Figures 6-28, -29 and -30 describe the system. The cost factors and air cleaning costs are given in Tables 6-XII and -XIII for a 3,800 ft^3/min system operation at several concentrations of 4-methyl-2-pentanone or propanone.

The results show a lower air cleaning cost for 4-methyl-2-pentanone (the higher boiling liquid) by the continuous-recycle system than by the stationary bed systems. At 100 and 500 ppm concentrations, the costs are \$0.46 and \$0.54/hr per 1,000 ft^3/min, respectively. For propanone, the air cleaning costs are the same, i.e., \$0.55/hr per 1,000 ft^3/min. In each case, the continuous-recycle system produces a separated liquid pollutant (or solvent) which may then be reused or disposed of by any means deemed best. The air cleaning cost by the stationary bed system leaves the pollutant dissolved in the steam condensate. When the stationary bed system is used with noncondensable gas regeneration plus incineration of desorbed vapors, the air cleaning cost rises to \$0.63/hr per 1,000 ft^3/min. The continuous recycle system appears more economical at the lower pollutant concentrations, although, admittedly there are also more uncertainties in the cost factors used in working up the estimates.

Adsorbents and Adsorbent Systems' Manufacturers and Vendors

Activated Carbons

Table 6-XIV lists under each manufacturer's name the trade name, properties and selling price range of gas-phase carbons that are suitable for air pollution control applications. For most applications, the interest is in the coarse mesh sizes, 4 to 6 or 4 to 10, although in some toxic chemical, biological and radiological applications the finer 12 to 30 mesh is also used. The density range 0.45 to 0.50 or 28 to 31 lb/ft^3 appears to be fairly standard. In regard to adsorptive capacity, this density range is optimum when measurements are made on the unit carbon volume basis. Some carbons are pelletized and others granular. The pelletized carbons tend to be slightly harder and, because of the narrower mesh size range, usually offer less resistance to airflow than granular carbons of equivalent mean granular diameter. In regard to adsorptive capacity, as measured by the CCl_4 activity, most carbons fall in the range 50% to 60%; see test procedure in Appendix D. The CCl_4 activity essentially measures the micropore volume of pores less than 30 Å in diameter; see Chapter 4, Activated Carbon Pore Size Distribution for significance of CCl_4 activity in regard to porosity.

Table 6-XII Estimated Operating Cost, Continuous Recycle Unit Including Solvent Recovery

Design basis

Airflow:	3800 ft³/min at 77°F
Carbon:	Granular BPL V
Operation:	8 hr/da, 2080 hr/yr
Solvent:	4-methyl-2-pentanone
Regeneration:	Continuous, internal air recycle 250 ft³/min at 250°F for 100 ppm 600 ft³/min at 250°F for 500 ppm
Solvent recovery:	Condensation via refrigeration at 0°F

Concentration	100 ppm	500 ppm
Installed equipment cost	$17,600	$18,700
Operating costs, $/yr		
Power at $0.015 kwh	1,130	1,620
Operating labor at $10/hr	300	300
Carbon replacement (5-yr life)	70	70
Maintenance, 2% of invest.	350	375
Depreciation, (10-yr life)	1,760	1,870
Total	3,610	4,235
$/hr per 1,000 ft³/min	0.46	0.54
Solvent recovered, 90% efficient, lbs/yr	10,900	54,500
Value of solvent recovered @ $0.135/lb, $	1,470	7,350

Table 6-XIII Estimated Operating Cost, Continuous Recycle Unit with Concentration of Pollutant for Subsequent Recovery or Disposal

Design basis

Airflow: 3800 ft³/min at 77°F
Carbon: 4 to 10 mesh granular BPL V type
Operation: 8 hr/da, 2080 hr/yr
Regeneration: Continuous, internal air recycle, 250 ft³/min at 250°F

Pollutant	4-methyl-2-pentanone	Acetone		
Concentration, ppm	10	10	100	300
Purge vent, ft³/min	12	5.1	51	153
Purge concentration, ppm	3,250	7,500	7,500	7,500
Purge vent concentration, % LEL	25	25	25	25
Installed equipment cost, $	16,500	17,600	17,600	19,800
Operating cost, $/yr				
Power at $0.015/kwh	960	1,690	1,830	1,830
Operating labor at $10/hr	300	300	300	300
Carbon replacement, (5-yr life)	70	70	70	70
Maintenance, 2% of investment	330	350	350	400
Depreciation, (10-yr life)	1,650	1,760	1,760	1,980
Total	3,310	4,170	4,310	4,580
$/hr per 1000 ft³/min	0.42	0.53	0.55	0.58

Table 6-XIV Activated Carbon Suitable for Air Pollution Control Applications

Trade name	Mesh size U.S. sieve No.	Bulk density, g/cm^3	Surface area, m^2/g	CCl_4 activity, %	Selling price, ¢/lb
American Norit Company, Inc.					
Norit RB I	Pellet 16x20	0.42-0.45	900-1000		
Norit RB II	" 8x12	"	"		
Norit RB III	" 6x8	"	"		
Norit RB IV	" 4x6	"	"		
Barnebey Cheney					
BC-BD	gran. ---	---		---	---
BC-G1	" 6x14	0.39		100	CA 90-100
Information on other grades not available					
Pittsburgh Activated Carbon					
PAC PCB	gran. 4x10	0.45	1150-1250	60	58-63
(coconut shell)	" 6x16				58-63
	12x30				55-58
PAC BPL	gran. 4x10	0.5	1050-1150	60-65	44-49
(coal base)	" 6x16		"		"
	" 12x30		"		"

Table 6-XIV (continued)

Trade name	Mesh size U.S. sieve No.		Bulk density, g/cm^3	Surface area, m^2/g	CCl_4 activity, %	Selling price, ¢/lb
Union Carbide Corporation						
Columbia NXC	pellet	4x6	0.48		60	
	"	6x8	0.48			
Columbia 3LXC	pellet	4x6	0.50		50	42-46
	"	6x8	0.50		50	41-45
	"	8x10	0.50		50	41-45
Columbia SXWC	pellet	4x6	0.45		65	90-94
	"	6x8	0.45		65	85-89
Columbia ACC	gran.	6x14	0.51		65	59-63
Columbia JXC	pellet	4x6	0.48		60	48-52
	"	6x8	0.48		60	47-51
	"	8x10	0.50		60	47-51
Westvaco						
Nuchar WV-H	gran.	6x16	0.48	1000	60	44-47
WV-H	"	12x30	0.48		60	44-47
Witco Chemical Co.						
Witco 235	gran.	12x20	0.56	930		
164	"	6x12	0.46	1200		
256	"	4x10	0.45	1250		
337	"	6x16	0.45	1300		
249	"	80x400	0.32	1400		
360	"	12x20	0.38	1800		

Very significant information regarding a carbon would be its generalized adsorption isotherm or isotherms; the type of isotherm referred to are shown in Figure 4-11 and -12. Cost estimates made on different types of carbons show that a carbon with a steep sloped isotherm is better suited for solvent recovery or adsorption-regeneration when adsorption occurs at high concentrations. Carbons with a small slope are better suited for poorly adsorbed pollutants or adsorption at very low concentrations, i.e., adsorption at large A values. In Figure 4-11, the BPL VI carbon would be more effective for adsorption at a very low concentration than the S154. On carbon weight basis S154 would be more effective than BPL V for solvent recovery. However, because of the low density of S154 much of the advantage of S154 cancels out when comparisons are based on equivalent volumes.

The addresses of the carbon manufacturers are as follows:

American Norit Company, Inc.
Jacksonville, Florida

Barnebey-Cheney
Cassidy at 8th
Columbus, Ohio 43219

Pittsburgh Activated Carbon
Division of Calgon Corporation
Calgon Center, Box 1346
Pittsburgh, Pa. 15230

Union Carbide Corporation
Carbon Products Division
270 Park Avenue
New York, N.Y. 10017

Westvaco
West Virginia Pulp and Paper
Chemical Division
299 Park Avenue
New York, New York 10017

Witco Chemical Company, Inc.
Activated Carbon Department
277 Park Avenue
New York, New York 10017

Two specialty items that are of interest to air pollution control are, (1) a bonded granular carbon panel manufactured by Pittsburgh Activated Carbon and (2) a particulate web manufactured by C.H. Dexter Corporation, One Elm Street, Windsor Locks, Connecticut 06096. The Pittsburgh procedure for bonding carbon granules gives a porous rigid structure that can be shaped into other forms aside from the panels. The bonding procedure does not significantly lower the carbon adsorptive capacity. The C.H. Dexter web consists of a thin flexible sheet of organic fibers to which are bonded powdered activated carbon. Fifty percent of the web weight is carbon.

Chemetron Corporation, Catalysts Division, P.O. Box 337, Louisville, Kentucky 40201, prepare specially treated carbons formulated for removal of sulfur compounds from synthesis and natural gas streams. The impregnated carbon is identified as G-32E catalyst.

Noncarbon Adsorbents

The following list presents the names of manufacturers of silica gel, activated alumina, molecular sieves and impregnated polar adsorbents. See Chapter 4, Types of Adsorbents for discussion of adsorptive properties.

Aluminum Company of America
1501 Alcoa Building
Pittsburgh, Pa. 15219

Product: Granular activated alumina, grades F-1, F-5, F-6 and H-181.

Davison Chemical
Division of W.R. Grace & Co.
101 North Charles St.
Baltimore, Md. 21203

Product: Granular silica gel and molecular sieves, types 3A, 4A, 5A, 2-100 and 13X.

Linde Company
Division of Union Carbide Corp.
Pleasant Valley Road & Rt. 38
Moorestown, New Jersey

Product: Molecular sieves, types 3A, 4A, 5A, 10X and 13X.

Marbon Division
Borg-Warner Corp.
Washington, West Virginia 26181

Product: Potassium permanganate impregnated alumina, Purafil trade name.

Sorption Systems

The following list presents the names of firms engaged in engineering and/or fabrications of various types of sorption systems used for air purification, solvent recovery, or specifically for control of air pollution.

Barnebey-Cheney
Cassidy at 8th
Columbus, Ohio 43219

System: Air purification and solvent recovery.

Cambridge Filter Corporation
7645 Seventh North Road
Syracuse, New York 13201

System: Air purification, pollution control - carbon pleated and flat panel types.

Conner Engineering Corporation
Division of Jenn-Air
Danbury, Connecticut

System: Air purification - pleated, panel, and canister type carbon beds.

Day & Zimmermann, Inc.
Philadelphia, Pa.

System: Carbon resorb with air or inert gas regeneration and incineration of desorbed vapor or readsorption in secondary adsorber.

Detrex Chemical Industries, Inc.
Box 501
Detroit, Michigan 48232

System: Solvent recovery - carbon stationary-beds with steam regeneration, hood ducts, freeboard chillers for degreasers.

Farr Company
2301 Rosecrans Ave.
El Segundo, California 90245

System: Air purification, pollution control.

Howard S. Caldwell Company
Caldwell Air-Park
P.O. Box 27
Baltimore, Ohio 43105

System: Air purification, canister and pleated panel types carbon beds.

Hoyt Manufacturing Corporation
251 Forge Road
Westport, Mass. 02790

System: Solvent recovery, stationary carbon bed with steam regeneration.

Marbon Division
Borg-Warner Corp.
Washington, West Virginia 26181

System: Air purification, potassium permanganate impregnated alumina panel type beds.

T. Melsheimer Co., Inc.
22610 South Western Ave.
Torrance, California 90501

System: Pollution control, multistage beds displaced at interval countercurrent to airflow, bed reactivated.

Mine Safety Appliances Co.
201 North Braddock Ave.
Pittsburgh, Pa. 15208

System: Air purification, pollution control-carbon pleated and flat panel types carbon beds.

RSE Incorporated
34875-23 Mile Rd.
New Baltimore, Michigan 48047

System: Air purification - carbon panel filters.

Steffey Metal Products, Inc.
Division of MacDonald Mfg. Co.
23-Mile at Sass Road
New Baltimore, Michigan 48047

System: Air purification - carbon panel filters.

Sutcliffe, Speakman and Co., Ltd.
P. O. Box 366
Bronxville, New York 10708

System: Solvent recovery, rotary bed continuous adsorber and dual stationary bed.

Vic Manufacturing Company
1620 Central Avenue, N.E.
Minneapolis, Minnesota 55413

System: Solvent recovery, dry cleaners with integrated solvent recovery, stationary bed with steam regeneration.

Vulcan Cincinnati, Inc.
1329 Arlington Street
Cincinnati, Ohio 45225

System: Solvent recovery, stationary carbon beds with steam regeneration.

7. Catalytic Incineration System

Basic Functions and Limitations

Oxidation and Reduction Functions

Catalysts can perform two basic functions useful in air-pollution control. The function already being used to considerable extent is the catalysis of oxidation reactions, as of carbon monoxide to carbon dioxide and hydrocarbons to carbon dioxide and water. The other function, which may have limited application to small sources control, is the reduction of nitric oxides to free nitrogen and oxygen.

Since the interest in air pollution control is the complete combustion of hydrocarbons, catalytic oxidation systems are regarded as incinerators, to emphasize a comparison to the competing thermal incinerators. A flow diagram of the basic catalytic incinerator is shown in Figure 7-1. The pollutant collection and blower system may be an existing ventilating system, to which the incinerator is attached, or installed to accommodate the incinerator. Preheat is required to raise the pollutant-air stream to the combustion-initiation temperature, which can vary from ambient temperature for oxidation of hydrogen to 750°C for oxidation of methane on a platinum alloy catalyst. Most pollutants of concern have oxidation-initiation temperatures in the range 400° to 600°F.

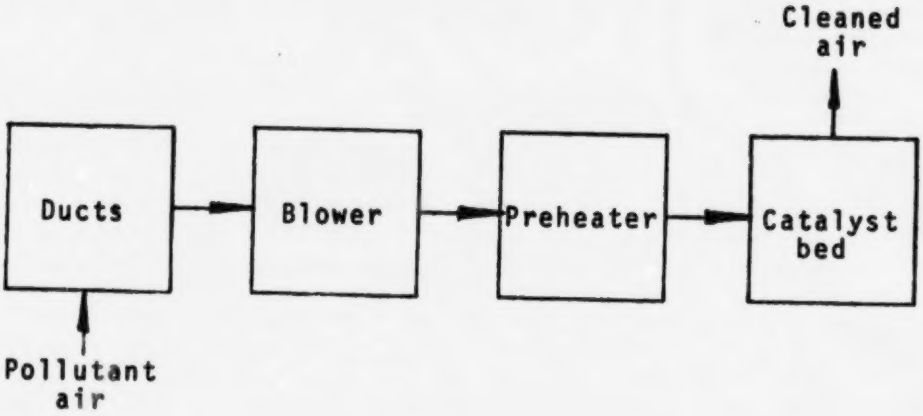


Figure 7-1 Basic Catalytic Incinerator Components

The types of catalysts best suited for catalytic combustion and reduction of pollutants are discussed in Chapter 5.

With correctly sized catalytic incinerators 90% to 98% of the pollutants are burned to the ultimate combustion products.

To improve the operating economics, more complex incinerators incorporate heat exchangers whereby the heat content of the effluent stream is used for preheating. When the combustible pollutant concentration of the influent stream is high, sufficient heat is generated for the incineration to become self sustaining. At low concentrations, additional fuel is required.

Advantages

The advantages (and disadvantages) of catalytic incineration are usually compared with thermal incineration. In this manual of package sorption devices its merits are also related to sorption devices and to a lesser extent to absorption devices or scrubbers. When the pollutant is a solvent with recovery value, the (nondestructive) sorption-type solvent recovery systems have a large economic advantage; see Chapter 6 - Comparative Costs for details. When the pollutant has no recovery value but is combustible to carbon dioxide and water vapor, the catalytic and thermal incinerators perform the same function. When incineration is advantageous over control by sorption devices, the advantages of catalytic incineration are related to thermal incineration.

The important advantage of catalytic incineration is the decreased reaction temperature. For efficient thermal incineration, furnace temperatures of 1200° to 1500°F are required while catalysts operate effectively in the 600° to 900°F range. From this single source, the economic assets are distributed through equipment, fuel and maintenance. Less refractory containers and supports are required which, in turn, reduce construction material and fabrication costs. The largest economic factor is the savings in fuel. Cost analyses of Hein (1964) favor catalytic oxidation 2 to 6 times over the thermal equivalent. The analyses as summarized in Figure 6-31 indicate that catalytic systems are favored by a factor of approximately 1.5.

An important advantage to catalytic incineration, and also of thermal incineration relative to sorption methods, is that they can control fumes from baking, roasting and varnish cooking operations which yield, in addition to solvents, high molecular weight polymeric decomposition products (considerably above 190 cm³/mol V_m). These high molecular-weight pollutants cannot be desorbed from the carbon on regeneration, thereby shortening the useful service life of the carbon.

Many processes emit the pollutant exhaust at elevated temperatures, as for example, coffee roasting. This factor is advantageous for catalytic and thermal incinerations when combustible pollutant concentration is low since it reduces or may eliminate the fuel requirements and reduces equipment costs, since heat exchangers are not required.

Disadvantages

The disadvantage of catalytic incineration relative to the thermal equivalent is the deactivation of the catalysts due to "poisoning". Deactivation or "poisoning" may occur through preferential adsorption of an undesirable or unreactive compound, physical erosion of the active surface sites, chemical reaction, or destruction of active surface sites by excessively high operating temperatures.

Most of the heavy metals, halogens, sulfur, phosphates and silicates will poison metal catalysts. The poisoning mechanisms vary among these examples, but each reduces the catalytic activity and results in higher operating costs. Trace concentrations of any of these poisons will reduce the catalyst life significantly. Operating life may be limited to months instead of years, which might be realized with a nonpoisoning atmosphere.

Particulates present in the pollutant airstream must be removed by filtration for both the catalytic incinerators and sorption systems to prevent possible poisoning of the catalysts or clogging the catalyst or adsorbent bed. In this respect some advantage can be credited to the thermal incinerator, since it can continue operations and, in some cases, realize complete combustion of the particulates.

A short-coming of both the catalytic and thermal incinerations is the effects produced by incomplete combustion. Oxidations occur through a series of steps producing various intermediate oxidation products which may be more undesirable than the original pollutant. An example of the possible range of intermediate products can be illustrated with the oxidation of butane, as follows:

Butane + $O_2 \longrightarrow$ Butanol, slight odor
Butanol + $O_2 \longrightarrow$ Butanal, malodor
Butanal + $O_2 \longrightarrow$ Butyric acid, nauseating
Butyric acid + $O_2 \longrightarrow 4CO_2 + 4H_2O$, odorless.

Temperature control must be maintained and the incinerator sized to minimize or avoid the production of intermediates.

Pollutant airstreams containing considerable amounts of nitrogenated, sulfurated, and/or halogenated hydrocarbons can produce unacceptably large amounts of NO_x, SO_x and hydrogen halides on incineration. Unless provisions are made to control the effluent acids, the alternative would be the sorption methods. In a relatively dry effluent free of SO_x and hydrogen halide the NO_x can be catalytically decomposed.

Some precautions must also be taken in the selection of oxidation parameters to prevent explosion or flashback in gas streams having high pollutant concentrations. Complete combustion is more probable in these systems, and it is also possible to extract some heat from the excess heat of combustion. However, when temperatures are high and gas velocities low, conditions may be established for autoignition, flashback or explosion. As recommended for the adsorption systems, the upper concentration limit is 25% of LEL for general operations. In some specific cases where the concentration is stable (i.e., does not fluctuate) or where protective monitoring instruments and controls are used, the allowable concentration can be increased to 40% of LEL.

Large variations in pollutant concentration produce operational problems which, however, can be corrected, at a cost, with instrumentation and other auxiliary equipment. Increases in concentration above the concentration for which the catalytic incinerator was designed may cause the catalyst temperature to rise to the point where the catalyst becomes deactivated. Conversely, a decrease in concentration can lower the combustion efficiency below the design level unless additional fuel is added.

Potential Applications

A number of applications of catalytic incineration in air pollution control are noted in Chapter 1, - the emission sources being the spray booths, surface coating baking ovens, drying ovens used in metal coating and lithographic operations, coffee roasting, meat smokehouses and meat rendering. Incineration systems based on noble metal coatings, which will correct air pollution from a number of industrial processes, are being advertized (Universal Oil Products). The list contains forty-one specific processes, most of them fitting into the general industries listed above or in the list of Other Emission Sources in Chapter 1.

Trace contaminant removal is also a significant factor in the preparation of controlled environments. Air and space vehicle compartments, medical and biological test stations and many welding and cleaning operations require use of gases cleaned of trace impurities. Catalysis is used in many of these applications to provide fast, efficient purification.

The choice of control system depends on the balance of advantages and disadvantages of the systems for the pollutant emission under consideration.

System Design Parameters

As in the application of adsorption systems for pollution control (Chapter 6), the engineer will be required to adapt the catalytic incinerators in most cases to processes already in operation. These processes have been developed and also optimized for better production efficiency without much consideration given to air pollution. As air pollution control regulations have been coming into effect one approach has been to increase the exhaust volume to decrease pollutant concentration and another has been to make minor changes in solvent mixtures by leaving out components that are specially objectionable. The result is that the conditions are not optimum for pollution control. When a new installation is being considered, the opportunity exists for the machinery manufacturer and process engineer to optimize the overall operations to include pollution control and thereby attain its most economical usage.

The first source of data for design and operating specifications is the properties of the pollutant exhaust gas from the process. The important properties to be considered are:

Flow rate
Type of pollutant
Pollutant concentration
Temperature
Presence, type and concentration of poisons
Presence, type and concentration of particulates.

An important decision is the efficiency that should be sought in the incineration process. Complete combustion of the pollutant is not practical; however, 99% efficiency is attainable under favorable conditions. Efficiencies during continued operation gradually decrease, hence high efficiencies are usually attainable only with a fresh catalyst.

Important factors concerning the catalyst and the incinerator operation to meet the desired or required goals of efficiency are as follows:

Chemical make-up of catalyst
Catalyst surface area
Catalyst support
Operating temperature
Reaction kinetics
Resistance of catalyst bed to gas flow
Residence time of gas in catalyst bed.

In this area the mathematical expressions, 3, 4, 5, 6 and 10 presented in Chapter 5 are used for the incinerator design purposes. Specific installations may provide additional data or operating experience useful to finalizing the design.

The effects of the operating variables on the incinerator operation are discussed further in the following text.

Type of Catalyst

Catalyst properties and classifications are reviewed in Chapter 5. In general, the noble metals are the most efficient for hydrocarbon combustion. The oxides of transition metals follow in the order Co>Cr>Mn>Cu>Ni>V>Fe>Ti>Zn.

Transition metal oxide catalysts are more easily poisoned than the noble metals, but their lower cost and greater selectivity could be advantageous.

Catalysts of tested performance and reliability are available from various manufacturers, but their compositions and preparations are either patented or proprietary information. Air pollution control systems usually require the treatment of heterogenous mixtures (gas mixtures, catalyst poisons and particulates) which make catalyst selection difficult. The selection can best be made by the catalyst manufacturer after all the other operating parameters have been determined for the particular application.

Type of Pollutant

The chemical nature of the gaseous pollutant determines not only the catalyst selection but also the ease with which it can be oxidized. According to Stein (1960), the ease of oxidation follows the patterns given below:

Branched hydrocarbons are more difficult to oxidize than normal hydrocarbons.

Ease of oxidation increases with molecular weight in a homologous series.

Unsaturated aliphatic hydrocarbons are more easily oxidized than the corresponding paraffins, and susceptibility to oxidation increases with increasing unsaturation.

Open-chain compounds are more easily oxidized than cyclic ones having the same number of carbon atoms.

Aromatic compounds, regardless of substitution, appear to be easily oxidized over most catalysts.

Oxygenated aliphatics and aromatics are equal to or more readily oxidized than the parent compounds.

Organic nitrogen compounds, such as pyridine, morphaline and monoethanolamine, produce essentially theoretical carbon dioxide and water with small amounts of nitrous oxide.

The minimum oxidation-initiation temperature or, more important, the temperature at which 90% conversion occurs measures the ease of oxidation of a vapor in air. Table 7-I records these temperatures and also autoignition temperatures for some of the known air pollutants emitted by small stationary sources. These temperatures are approximate and apply to a noble metal catalyst at flows maintained to give comparable residence times.

For a pollutant airstream at concentrations high enough for the catalytic oxidation to be self sustaining, a portion of the catalyst bed must be heated to the oxidation initiation temperature, as by preheating the airstream. The combustion of the pollutant then supplies the heat to raise the combustion process to more efficient temperature levels and preheat may no longer be required. At low concentrations essentially all the heat must be supplied by added fuel to maintain the catalyst at temperatures where catalytic efficiency is maintained at 90% or better. Ninety percent and higher efficiencies would be maintained at 800°F for most air pollutants of concern. Some of the acetates and ketones would require temperatures at the 900°F level.

In the incineration of flammable vapors operational safety is an important consideration. When the autoignition temperature is lower than catalytic operating temperature, as for some of the normal hydrocarbons and ethyl acetate, (in Table 7-I) a flash-back or explosion would occur if the concentration were allowed to rise to the lower explosive

Table 7-I Minimum Temperature for Initiating Catalytic Oxidation and Autoignition of Organic Pollutant Vapors in Air, Degrees Fahrenheit

Pollutant vapor	Catalytic oxidation (1)	Catalytic oxidation (2)	Auto-ignition	90% catalytic conversion
Methane	760	800	999	932
Ethane	680		959	
Propane	650	660	870	1065
Butane	570	570	806	750
Pentane	590		495	
Hexane	630		433	725
Heptane	490		433	520
Octane	490		428	
Decane	500		406	
Dodecane	540		399	
Hydrogen		32	1076	250
Carbon monoxide		300	1204	500
Ethyne		280	365	
Benzene	440	500	1076	575
Toluene	460		896	575
2-Butanone	550		960	660
4-Methyl-2-pentanone	560			860
Ethanol	540		793	575
Ethyl acetate	730		800	880(80%)
o-Xylene	470	570	924	575

(1) Suter (1955)
(2) Romeo (1962)

limit (LEL). Table C-II in Appendix C records the autoignition temperatures, lower explosive limits and also the heats of combustion and molecular weights of some of the identified small source pollutants. Dangerous concentration levels for propane, hexane, heptane and ethyl acetate are 21,000, 11,000, 12,000 and 22,000 ppm respectively.

The presence of CO_2 and H_2O in the pollutant stream have an inhibiting effect on hydrocarbon oxidation, while CO promotes their oxidation as was demonstrated by Klimisch (1968) with propene and hexane on alumina supported copper oxide catalysts.

Chemical composition of pollutants also affects the nature of combustion products. This is important in catalytic systems where partial oxidation is always a possibility. The desired products would have no toxic or odiferous nature.

Pollutant Concentration

The effects produced by the pollutant concentration are closely involved with the heat content of the air and heat of combustion of the pollutant. These three factors determine the amount of added fuel and/or recycled heat required to maintain the optimum operating temperature level. The main heating load is the heat content of the air, after steady state has been attained. Lesser heat losses occur through the incinerator shell. To raise the air temperature from 60°F base temperature to 600° to 900°F (the effective catalyst operating temperature range) requires 10.5 to 16.5 Btu/(std) ft^3. (For thermal incineration operated in the 1200° to 1500°F range, the required heat input is 22.5 to 28.5 Btu/(std) ft^3, or approximately twice as much.)

Table 7-II presents estimated concentrations at which some of the more frequently encountered air pollutants would be self sustaining at the 90% efficiency level. These estimated concentrations do not cover heat losses through the incinerator shell and also apply to incinerators without heat recycle. In each case the concentration is near the 25% LEL, hence self sustaining catalytic combustions are feasible at safe concentration levels.

When the pollutant concentrations are low, additional heat input is required to maintain high conversion efficiencies. . Table 7-III presents the calculated amounts of heat input from pollutant combustion at varied concentrations, assuming 100% conversion to CO_2 and H_2O. The difference between the total heating load, in the 10.5 to 16.5 Btu/ft^3 of air range, and the Btu/ft^3 given in Table 7-III at each concentration is the amount of additional heat required.

At concentration levels up to 100 ppm, 95% or more of the required heat input comes from the preheat source. Fluctuations in concentrations, which normally occur in many industrial processes, would have very little effect on the steady operation of the incinerator. Fluctuations

Table 7-II Pollutant Concentration Required for Self-Sustained Catalytic Combustion at 90% Conversion Level

Pollutant vapor	Heat of combustion, Btu/ft³	90% conversion temp. °F	Concentration, ppm	25% of LEL, ppm
Hexane	5,000	700	3,000	2,700
Toluene	4,500	600	2,500	3,000
4-Methyl-2-pentanone	4,200	850	4,000	3,500
Ethyl acetate	2,700	900 (80%)	7,500	5,500
Propane	2,600	1100	8,500	5,200
Propanone	2,000	800 (est)	8,000	7,500
Ethanol	1,600	600	7,000	8,200
Natural gas(methane)	1,000	900	19,000	12,500

Table 7-III Heat Input from Pollutant Combustion at Varied Concentrations

Pollutant vapor	Heat input, Btu/ft³ (stp)				
Conc., ppm	1	10	100	1000	3000
Hexane	0.0050	0.050	0.50	5.0	15
Toluene	0.0045	0.045	0.45	4.5	13
4-Methyl-2-pentanone	0.0042	0.042	0.42	4.2	13.5
Ethyl acetate	0.0027	0.027	0.27	2.7	8.0
Propane	0.0026	0.026	0.26	2.6	8.0
Propanone	0.0021	0.021	0.21	2.1	6.3
Ethanol	0.0017	0.017	0.17	1.7	5.1
Natural gas(methane)	0.0010	0.010	0.10	1.0	3.0

in pollutant concentrations at levels higher than 1000 ppm can cause catalyst overheating or underheating unless compensating adjustments are made to the preheat input rate. At the low concentration, the catalytic incinerator operation is the most stable but the more costly in fuel consumption.

Operating Temperature

The operating temperature - i.e., catalyst bed temperature - influences both the efficiency and life of the catalyst. If this temperature is below the initiation temperature, no oxidation occurs; but above the initiation temperature, the oxidation efficiency increases as the operating temperature increases.

The two major catalyst types - noble metal and metal oxide catalysts - exhibit wide differences in this operating parameter. Transition metal oxide catalysts usually operate in the temperature range 200° to 600° Farenheit, while noble metal catalysts operate in the temperature range 400° to 1200°F.

The optimum operating temperatures reflect these differences (300° to 400°F for metal oxides and 750° to 1050°F for noble metals). Deterioration and deactivation of the catalysts also follow this pattern. Operating transition metal catalysts above 600°F limits their effective catalytic life to the point where replacement costs may become a limiting factor. Similarly, noble metal catalyst lives are limited when operating above 1200°F.

Figure 7-2 illustrates the general pattern of temperature effect on conversion efficiency. An important characteristic of the temperature effect is that the efficiency approaches the 100% level gradually; a large temperature rise is often indicated to increase the efficiency from 90% to 100%. The curve presented in Figure 7-2 is based on data of Miller (1967).

The operating temperature also has an influence on the products formed. Partial oxidation occurs to a greater degree at low temperatures, producing undesirable combustion products. Such products would completely nullify the desired benefits of the pollution control device since, in most cases, these products are more photochemically reactive and more odiferous than the original pollutants.

In the operation of the catalytic incinerator, the temperature of the pollutant airstream is an important economic factor. When the pollutant is below the concentration

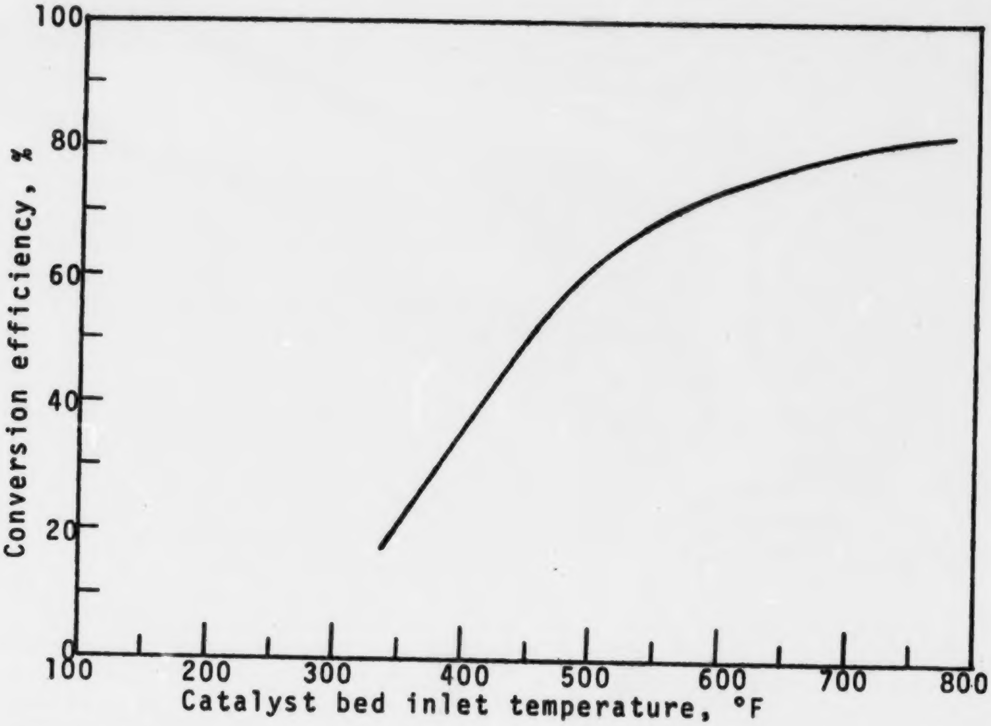


Figure 7-2 Effect of Temperature on Catalytic Combustion of 2-Butanone on Pt/alumina, 4" Depth Honeycomb Bed, 80,000 Space Velocity and 10% LEL Concentration

required to sustain the temperature at levels where high efficiencies are attained, a hot pollutant airstream can greatly minimize or avoid the need for additional fuel or the expense of installing heat exchangers.

Residence Time

For a given pollution control problem the required residence time determines the catalyst bed size. The residence time, required to attain a high conversion efficiency, depends on the reaction rate which in turn is a function of the chemical composition of the pollutant, its concentration, the type of catalyst, and the operating temperature. The composition and concentration of the pollutant, and also the pollutant airflow rate are fixed variables determined by the emission source. After selection of the catalyst (best determined by the catalyst manufacturer), the operating

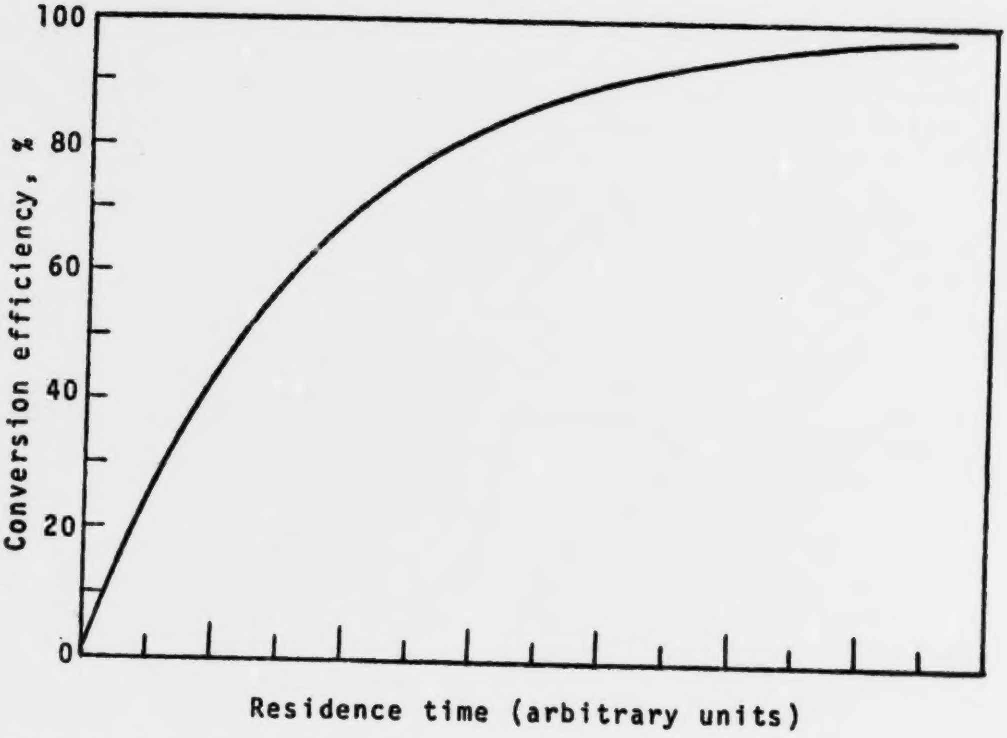


Figure 7-3 Effect of Residence Time on Catalytic Combustion Conversion Efficiency

temperature and residence time become the two important variables to be optimized for minimum operating cost of the incineration.

As discussed under Operating Temperature, the conversion efficiency increases at a diminishing rate with temperature rise above the 90% level. In a similar manner, the conversion efficiency also increases at a diminishing rate with residence time. At lower operating temperatures - those safest from temperature deactivation - the conversion efficiency can be maintained by increasing residence time (i.e., increased bed size for a fixed flow rate). Figure 7-3 shows this effect in arbitrary residence time units. The limiting factor is the cost of the catalyst. As temperature is increased the residence time can be decreased. In this case, the limiting factor is the deactivation of the catalysts at the higher temperatures.

The curve in Figure 7-3 follows the equation:

$$\% \text{ conversion} = 100 - f^{n} \qquad (7\text{-}1)$$

where f is the percentage of influent concentration penetrating a catalyst layer and n is the number of layers. The residence time is proportional to the number of layers.

When the catalyzed reaction is first order with respect to the pollutant species, Equation 5-5 reduces to,

$$C/C_{o} = e^{-Kt} \qquad (7\text{-}2)$$

where C/C_o is equivalent to f in Equation 7-1. Then the efficiency of a catalytic incineration can be represented by the equation:

$$\text{fraction converted} = 1 - [e^{-Kt}]^{n}. \qquad (7\text{-}3)$$

The reaction rate constant, K, and residence time, t, for layers or individual cells of catalysts, are generally known by the manufacturer. Equation 7-3 shows that the conversion efficiency increases exponentially with K and t. Similar theoretical correlations can be made using Equations 5-6 and 5-10.

When Equation 5-10 is used, a catalyst bed length-to-diameter ratio is also shown to influence the efficiency. As seen in Equations 7-2 and -3 above the conversion efficiency increases with the residence time per individual cell and the number of cells. Efficiency increase, by enlargement of the bed, can be done by adding the cells in series to increase bed length or in parrallel to increase bed diameter, or a combination of the two. When length alone is increased, the flow velocity remains constant, while an increase in diameter produces a decrease in flow velocity. K decreases slightly with decreased flow velocity, but because it is in the exponent, this small change is magnified in its effect on efficiency. Equation 7-3 then strictly applies when the bed is enlarged by adding cells in series. The limiting factor in this case is the resistance to airflow. In practice the pressure drop is usually held below 12 in. of H_2O. If the bed volume is enlarged by increasing the diameter to avoid excessive pressure drop, the limiting factor is the reduction in K.

Operating Costs

The economic analysis of the catalytic incinerator operations include the following costs:

Fixed capital
Depreciation
Operating labor
Maintenance
Electrical power
Fuel.

To establish the operating costs on a basis that can be compared to those of the thermal incinerators and carbon resorb systems, they are worked up as \$/hr per 1,000 ft^3/min of polluted air that are cleaned.

Equipment

Installed costs vary between \$3,500 and \$6,000 per 1,000 ft^3/min (stp) air handling capacity. The higher end of the range includes costs for heat exchangers, and filters for particulate removal, and also reflects the costs of more expensive catalysts. As the size is increased, the cost per unit air handling capacity decreases to some extent but, for the range 2,000 to 10,000 ft^3/min flow capacities, the cost per 1,000 ft^3/min was assumed to be essentially constant for the comparative operating cost estimates reported in Chapter 6. The higher \$6,000 figure was used at pollutant concentrations below the self sustaining concentrations (below about 3,000 ppm), since heat exchangers give a decided operating cost reduction.

Depreciation

A 10-year depreciation rate is often used by analysts making cost comparisons with thermal incineration. Some variation in deterioration rate will occur depending on whether the incinerator is in intermittent or continuous service, i.e., 8 or 24 hr/da.

Operating Labor

Operating labor costs for catalytic incinerators are relatively small after the incinerator has been put into operation; this is also true of thermal incinerators and carbon resorb systems. A low level of operating cost has been estimated on the basis of 5 min of labor per 8-hr shift for each 1,000 ft^3/min capacity (Hein 1964).

Maintenance

Yearly maintenance costs have been estimated by some analysts on the basis of 10% of the initial incinerator cost (Hein 1964). Other methods can consist of periodic catalyst-replacement cost combined with a lower percentage rate of the initial incinerator cost.

Electrical Power

The main electrical power consumer is the air circulating fan or blower. The kilowatts to move 1,000 ft^3/min of air through an incinerator or carbon resorb bed can vary from 2.5 to 4 in the control systems of 2,000 to 10,000 ft^3/min airflow capacities. Local electrical costs per kilowatt hour will determine the power cost.

Fuel

Fuel costs, using natural gas for preheat purposes, are approximately \$0.60 per 10^6 Btu. At pollutant concentrations below the self sustaining level, preheat is required at varied amounts depending on the type of pollutant and pollutant concentration. The amount of preheat required can be estimated from the calculated data given in Tables 7-II and 7-III for several frequently encountered pollutants. The self sustaining concentrations of Table 7-II were calculated for a 60°F base temperature for the pollutant airstream. At higher pollutant airstream temperatures, if heat exchangers are utilized, the preheat requirements can be considerably less.

Auxiliary Equipment

Before the catalytic incinerator proper can be put into operation, a number of auxiliary pieces of equipment are required for its efficient and safe operation. These are listed in Table 7-IV.

Table 7-IV Auxiliary Equipment for Catalytic Incinerators

Ducts and supports
Blowers
Filters
Scrubbers
Preheaters
Heat exchangers
Monitors
Controls

In the previous text the blowers, filters, heaters and heat exchangers, of necessity, have been brought into the discussion, but more can be said of their functions.

Ducts and Supports

Ducts to direct the pollutant from the emission source to the incinerator are an economic necessity. Incineration of the total ventilation airstream is invariably too costly to be considered. By ducting, the quantity of air to be treated is kept smaller and also the concentration of pollutants is maintained higher, thereby reducing the required fuel costs.

In existing operations, the retrofitting of the ducts, the catalytic unit and its supports can be a problem. Industrial processes are often designed to conserve space, with little room remaining for later installation of pollution control systems.

Filters and Scrubbers

Filters are usually necessary to protect the catalyst bed from particulates in the airstream because particulates may: (1) poison the catalyst, (2) cause deactivation by erosion or coating or (3) in the case of a granular catalyst bed cause increase in flow resistance. Removal of particulates from the airstream is also done by scrubbing with water. This procedure is feasible at ambient temperatures, at the 77°F level, where the water vapor content will then be established at about 4%. Efficient demisters would also be required to keep the water content low, since water vapor at higher concentrations interferes with the catalysis; higher temperatures would be required.

Secondary filtration, after the catalyst, may also be required for some catalysts such as packed or fluid beds.

Blowers

Air movement produced by convection or ventilating fans cannot effectively overcome the resistance of the catalyst bed and auxiliaries such as heat exchangers or preheaters. Pressure drops at the 12 in. of H_2O level are encountered with some catalyst beds. Blowers are required for the exclusive operation of the incinerator.

Preheaters

Preheaters, auxiliary fuel and external heating may all be used intermittently. Unless the pollutant airstream temperature is already at the initiation temperature, extra heating is required to initiate the combustion. Subsequent heat or auxiliary fuel requirements depend on the fuel value of the pollutants.

Preheaters may be of the heat exchanger type where the pollutant airstream does not come in direct contact with the gas burner, or it can be a direct flame type. The latter raises the water content of the pollutant airstream, which with some catalysts may reduce their activity.

Heat Exchangers

The effluent gas stream from the incinerator is usually at temperatures ranging from 600° to 900°F. By use of a heat exchanger a part of this heat energy becomes available for preheating the influent air to the incinerator or for other purposes such as steam generation, space heating or process heating. When the pollutant control is a steady operation, the heat recovery for secondary uses may make the pollutant control a profitable operation. This would be the case when the pollutant concentration is at the self sustaining level or at lower concentration when the influent is at elevated temperatures.

The cost of the exchanger can be 25% to 40% of the total cost of the incinerator, but a heat exchanger operating at 50% recovery used for preheat reduces the fuel cost by about 50% at low pollutant concentrations. The estimated operating cost, given in Chapter 6, is \$0.94/hr per 1,000 ft^3/min with a heat exchanger, while without an exchanger it is \$1.30/hr per 1,000 ft^3/min.

Figures 7-4, 7-5 and 7-6 show diagrams of incinerators in the various combinations of preheaters and heat exchangers.

Monitors and Controls

Some type of measurement is necessary to determine the efficiency level at which the catalyst is working. A number of alternative methods are available which may be placed in seven general categories.

Component Identification - Although it is usually a temporary arrangement, it is advisable to run complete analyses of the exhaust stream to assure the removal of all pollutant species. This will require the use of hydrocarbon, CO, SO_x and NO_x analyses, which can be done by gas chromatography. Usually this is done at the beginning of operation or during a pilot run to assure the unit is performing to design.

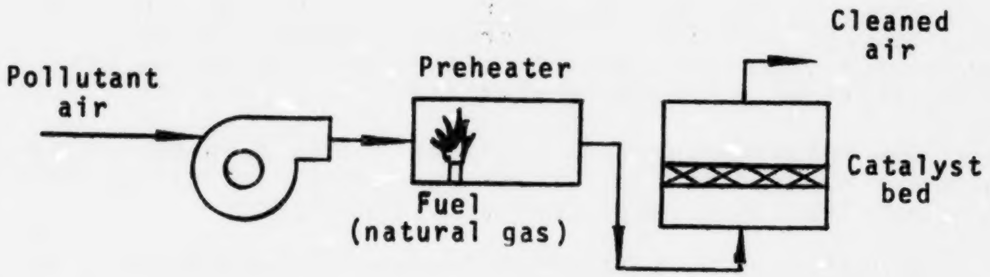


Figure 7-4 Basic Catalytic Incinerator With Gas Burner to Supply Preheat

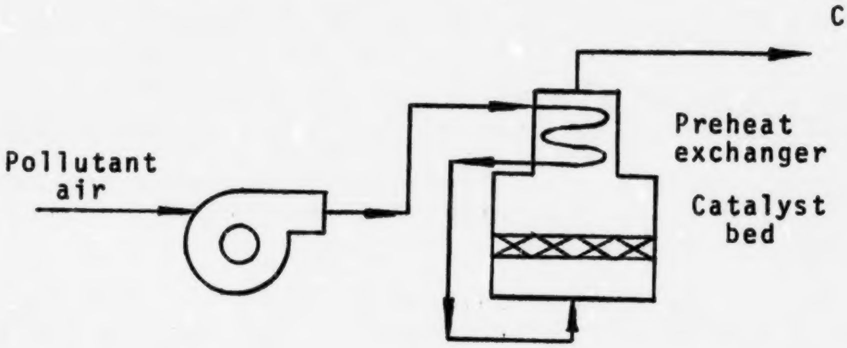


Figure 7-5 Catalytic Incinerator With Heat Exchanger to Supply Preheat

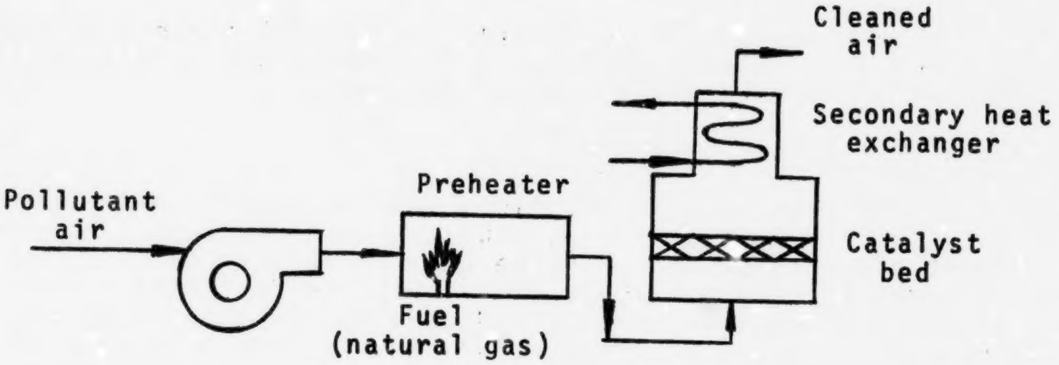


Figure 7-6 Catalytic Incinerator With Burner to Supply Preheat and Secondary Exchanger to Recover Heat for Process Use

Total Hydrocarbon Analyzers - These monitors may be used to supply continuous information concerning the concentration of hydrocarbons in either the process exhaust or catalytically treated gas streams.

Dew Point Measurement - Either hydrocarbon pollutant or water-product dew points may be used to follow the changes in concentration through the catalytic burner.

Temperature Measurement - Increased temperature with passage through the catalyst bed is an adequate test for determining if the catalyst is working.

Addition of a Tracer Compound - By addition of a hydrocarbon having a characteristic odor, cursory measurements are possible using olefactory sensitivities to the influent and exhaust gas streams.

Pressure Measurement - Pressure drop through the catalyst bed can be used to measure the attrition of the catalyst.

CO and CO_2 Measurement - Instrumental analyses are available for the continuous measuring of CO and CO_2 concentrations in flue gases.

Each of the analytical tools mentioned previously can be used to determine the deterioration of a catalytic burner and the time for maintenance. Here again, the degree of change necessary to indicate poor operation and efficiency depends upon the physical measurement and the catalyst used. Additional information on instrumentation is given in Chapter 8.

Equipment suppliers provide the control parameters and the amount of change that can be tolerated while retaining the 90% or higher efficiency as required.

Care of Incinerator

Some care must be exercised with catalytic incinerators, especially during start-up, shut-down and storage. The catalytic elements, or beds, must be kept clean and relatively dry in order to maintain their activity. The degree of sensitivity and required care will depend on the type of catalyst. Specific care and maintenance procedures should be provided by the manufacturer. In general though, exposure to hydrocarbon solvents and hot, moisture laden gases should be avoided.

Start-up

An initial heat-up period will usually precede the actual operation of any catalytic burner. A flow of clean air is passed through the system until it is equilibrated at the desired operating temperature.

This heat-up period provides a time to clean the system and check all analytical instruments used to control operation. It also assures the maximum efficiency of the catalyst from the initial hydrocarbon exposure which eliminates problems of partial oxidation of pollutants and possible deactivation by absorption or poisoning.

Maintenance

Little or no maintenance is required for normal operation of catalytic incinerators. When pollutant airstreams contain poisons or large variations in the pollutant concentration, both maintenance and operating problems increase. Catalytic activity must be rejuvenated at regular intervals by washing with water and/or heating while passing a nonpolluted airstream over the catalyst bed.

Storage

Shutdowns and storage also require the use of nonpolluted gas streams to cool the system and maintain a relatively dry atmosphere during storage. The catalyst-bed temperature is slowly reduced by decreasing the pollutant concentration and recirculating hot effluent so the bed will not experience a thermal shock.

Catalytic Equipment Manufacturers

Several manufacturers offer complete engineering technology for the analysis of the pollution problem and for the design and fabrication of the catalytic incinerator to correct the problem. Some manufacturers supply only catalysts. In either case the equipment supplier requires an analysis, as complete as possible, of the pollutant airstream to make the correct selection of the catalyst and to design and fabricate the incinerator. The following text describes some of the products sold by these manufacturers.

Universal Oil Products of Darien, Connecticut, manufactures eight basic types of pollution control equipment that can be modified to treat most process streams according to the results of analyses. The catalysts used are activated noble metals deposited on nickel alloy supports.

Oxy-catalyst, Incorporated of West Chester, Pennsylvania, markets catalytic oxidation systems for internal combustion engines and industrial processes. Their catalyst is a platinized alumina which resists thermal shock, poisons and clogging. Five different sizes are available for use as odor eliminators or catalytic incinerators.

Matthey-Bishop, Incorporated of Malvern, Pennsylvania, manufactures a new platinized ceramic honeycomb, designated THT. It is claimed to offer the advantages of low pressure drop, higher activity and attrition resistance in the combustion of many organic vapors.

Mine Safety Appliances Corporation of Pittsburgh, Pennsylvania, markets several sizes of catalytic oxidation units for the purification of aircraft cabins, liquid air separation plants and removal of hydraulic fluid vapors. The catalyst used is MSA "Hopcalite", which is an activated mixture of CuO and MnO_2. Catalyst life is designed for greater than 500 hours, but depends upon the type of service and pollutants. Economical replacement is facilitated by designing a replaceable catalytic unit and using this relatively inexpensive catalyst.

The Harshaw Chemical Company of Cleveland, Ohio, manufactures catalysts of all types for catalytic incinerators. Both metallic and oxide catalysts are made from V, Cu, Mo, Pt, Pd, Co, Ni, Mn, Sn, and Pb. They do not, however, design or fabricate complete incinerator units.

Chemetron Corporation, Catalysts Activity Division, of Louisville, Kentucky, manufactures Girdler Catalysts. Their G-43 catalyst combines Pt and Ni on an alumina support and is used commercially for removing methane, ethane, ethylene, carbon dioxide and nitrogen oxides.

Atlantic Research Corporation of Alexandria, Virginia, is a fabricator of catalytic incinerators but does not manufacture catalysts.

E. I. DuPont de Nemours & Co., Industrial and Biochemicals Department of Linden, New Jersey and Englehard Minerals and Chemicals of Newark, New Jersey, manufacture catalysts and also design and fabricate incinerators.

FECO, of Cleveland, Ohio 44105, custom designed catalytic units using catalysts supplied by duPont and Matthey-Bishop.

8. Pollutant Detection

Introduction

This section on pollutant detection presents the practical aspects of monitoring the input and effluent from a packaged sorbent device. The intent is to provide guidance for the designer and users of these purification devices in the selection of appropriate monitoring systems. It is obviously impossible to deal with each specific pollutant source due to the many different types of pollutants, pollutant emissions rates and emission standards. Therefore, the information which is presented is of a generalized nature although specific details are given on detection capabilities, sensitivities, interferences, costs and so on. With this information, the designer or user can evaluate his specific emission problem and select an optimum monitoring system based on the information presented herein.

This section on detection covers three primary areas relating to monitoring of emissions:

1. Methods of sampling gases
2. Techniques and instruments suitable for monitoring emissions
3. Recommended methods for specific classes of impurities

Basically, the method of sampling, the technique or instrument chosen and the reason for selecting a specific approach to emission monitoring will depend upon many factors including the type and quantity of emission, the size of the emission control device, the rationale for using the device and cost of monitoring equipment. All of these factors are interrelated and will require technical judgment on the selection of a pollutant monitoring system. In the case of large corporations, in-house capabilities may exist and can be called upon to make the necessary decisions. Conversely, the small businessman may have to resort to an outside consulting service in order to select an appropriate monitoring system.

Pollution monitoring is required first to determine whether an emission control device is necessary and secondly, if an emission control device is needed, to determine when the emission control device requires regeneration or replacement. The need to install an emission control device is dependent upon two primary criteria:

1. As an economic measure to recover and recycle solvents

2. As a required measure to meet federal, state or local emission standards.

Therefore, an organization or business must identify what emissions exist and the extent of these emissions.

In addition to actual analytical data, other information can be used to determine emission rates. Source evaluations for commercial processes rely on process flow sheets, mass balance data and specific process engineering experience to identify possible sources. This requires the examination and assimilation of data from several disciplines and technical personnel with appropriate backgrounds for evaluation and correlation. This type of approach to estimating emission rates has been described by Jacobs (1949) and Stern (1968). Small businesses can estimate emission rates in the same fashion. For example, the operator of a dry cleaning establishment keeps an inventory of the quantity of cleaning solvent which is purchased over a period of time. By equating the volume of solvent used with the time of operation, an emission rate can be estimated.

The character of a source may be significantly changed by certain mixtures of pollutants or secondary reactions, which are not readily apparent in the initial evaluation. Therefore, regardless of the accuracy with which the basic variables can be estimated, analytical characterization of the effluent will be required.

Methods of Sampling Gases

Sampling is generally divided into two basic categories:

1. Grab sampling

2. Continuous sampling

Regardless of which method is used, the objective is to acquire a sample which is representative of the emission in terms of both types and quantity of pollutant in the exhaust effluent.

Grab samples are instantaneous samples which are generally returned to the laboratory for chemical or instrumental analysis, while continuous sampling is usually associated with on-site instrumental analyses. Grab samples can be taken in evacuated glass, metal or plastic containers, with the restriction that the pollutant neither reacts with nor is absorbed by the container wall. Grab sampling is an acceptable means of acquiring a sample when the type and concentration of pollutant is relatively constant.

When the type of pollutant or pollutant concentration varies with time then grab sampling is of questionable value. In such cases, an integrated sample can be taken where a sample of the effluent gas is drawn through a suitable sample collector over a period of time. This type of sampling provides an average concentration of the pollutant over the scheduled time period. Integrated sampling has an inherent advantage in that trace contaminants are concentrated and thus the problem of measurement of pollutant concentration may be minimized. The disadvantages include the necessity of accessory equipment such as flowmeters, pumps and so on.

The time variable in grab or integrated sampling techniques is an important part of the entire analytical procedure. Most commercial manufacturing is done on a cyclic schedule or includes "batch processes" where the emissions and rate of release vary. The schedule of the process must be known and all samples identified concerning both time and location for accurate interpretation.

Continuous sampling is usually associated with direct-reading, instrumental systems. A sample of the effluent gas is drawn through the instrument with a pump, and a continuous readout is provided by the instrument. This type of sampling system has the advantages of continuous data display and minimization of direct labor costs in procurring a sample. Many instruments have a sampling system as an inherent component or a sampling system can be purchased as an accessory. For example, portable battery powered instruments to measure LEL have sampling pumps as part of the instrument package. Most industrial chromatographs are purchased with continuous sampling equipment.

The sampling procedure which is ultimately selected will be influenced by a number of factors. Samples will be taken to determine whether or not an emission control device is required. In this case, sampling and subsequent analysis on a contract basis with an analytical services laboratory is frequently the best route to follow. If the evaluation is to be performed in-house, the type of sampling system used should be simple and inexpensive. Grab samples will generally suffice except in those cases where the rate and quantity of pollutants vary to an extreme degree over short periods of time.

If an emission control device is deemed necessary, then a judgment must be made on the type and complexity of the sampling system. This will depend upon many variables, as stated earlier, and the selection of a specific sampling system will have to be made on the basis of these factors.

Techniques and Instruments for Monitoring

Introduction

A discussion of the various pollutants amenable to removal by either sorption or catalytic combustion was presented in Chapter 1. These pollutants cover a multitude of chemical groupings exhibiting various physical and chemical properties. In most cases, the pollutants which have been categorized for potential removal by sorptive or catalytic devices are hydrocarbons. The specific type of hydrocarbons ranges from straight chain configurations to those with various functional groups attached to the hydrocarbon chain. Selection of an appropriate monitoring device or technique will depend upon the specific characteristics of a given pollutant. For example, straight chain hydrocarbons will likely dictate that a hydrogen flame ionization or thermal-conductivity detector be used, while chlorinated hydrocarbons may be identified more selectively by the use of an electron capture detector. Functional groups containing phosphorous or sulfur can be measured at low levels using a flame photometric method.

Instruments and analytical techniques are classified according to the specific physical or chemical characteristics which are measured. In general, these can be classified into the four major categories shown in Table 8-I; subdivisions within these categories are shown also. This listing is not meant to be all inclusive, but does represent the most likely means of detecting and measuring pollutants in gaseous effluents.

The analytical requirements of various pollution sources have encouraged the development of a myriad of analytical methods of varying degrees of relevancy for any particular application. Compilations such as published by Jacobs (1949),

Table 8-I Classification of Analytical Methods

I. Thermometric Instruments
   - A. Thermal conductivity
   - B. Catalytic combustion

II. Electrometric Instruments
   - A. Flame ionization
   - B. Ionization
   - C. Electrical conductivity

III. Spectrometric Instruments
   - A. Visible spectrum
     - 1. Interferometric
     - 2. Spectographic
   - B. Ultraviolet spectrum
     - 1. Ultraviolet photometric
     - 2. Ultraviolet spectrometric
   - C. Infrared spectrum
     - 1. Infrared spectrophotometric
     - 2. Infrared

IV. Chemical Methods
   - A. Gravimetric
   - B. Titrimetric
   - C. Detector tubes

Stern (1968) and Ruch (1970) are a few of the exceptionally good references available for selecting an analytical method or instrument capable of measuring an air pollution sample accurately. The selection of a method or combination of methods required to obtain a desired accuracy should be made on the basis of best estimations for several parameters. These complex mixtures present individually unique problems compounded by the large variations in concentrations and possible interferences among the components.

In general, all pollution detection methods are judged on the basis of seven parameters (i.e., specificity, range, sensitivity, reliability, accuracy, maintenance and costs). Selection of a preferred method is made by optimizing the performance for each parameter and selecting the best compromise which is available for the individual gas sample.

Methods of Analysis

Detailed reviews of analytical methods for specific compounds have been published by Jacobs (1949, 1960, 1967), U.S. Public Health Service (1965), Stern (1968) and Ruch (1970). These authors provide excellent descriptions of the accuracy, interferences and actual procedures to measure specific compounds.

Table 8-II lists the general classes of pollutants which are most likely to require control devices, along with possible methods of measuring these pollutants, and the detection range. Costs are not included in this table since this factor varies among manufacturers and according to the accessories acquired with the monitoring device. Direct contact with a manufacturer will frequently provide valuable information on the instrumentation which is available for a specific application and the cost of a complete instrument package.

Thermal Conductivity - Automatic recording instruments are commercially available for the determination of gases and vapors based on their thermal conductivity. The absolute values of the thermal conductivity are seldom used for analytical purposes, but several selected values have been reported (Willard, 1958). The thermal conductivity of a gas mixture to be analyzed is usually compared with that of some reference gas, such as hydrogen, nitrogen, or wet or dry air.

A fine wire, usually platinum or some other metal or alloy with a high temperature coefficient or resistance, is stretched along the axis of a metal or glass cylinder.

Table 8-II Common Analytical Methods Used for Air Pollutant Detection

	Thermal conductivity	Catalytic combustion	Ionization Methods	Ultraviolet spectrophotometry
Hydrocarbons	100-10,000 ppm	1-1000 ppm 1-100% LEL	0-1 ppm 1-10,000 ppm	0-10 ppm 10-200 ppm
Oxygen-containing organics	100-10,000 ppm	1-100 ppm 1-100% LEL	1-10 ppm 10-1000 ppm	0-10 ppm 10-200 ppm
Halogenated organics	100-10,000 ppm		0-10 ppm 10-1000 ppm	
Inorganic oxides	100-10,000 ppm		1-100 ppm	
Odors				
Aromatic hydrocarbons	100-10,000 ppm	1-1000 ppm 1-100% LEL	0-1 ppm 1-10,000 ppm	0-10 ppm 10-200 ppm
Polynuclear hydrocarbons				0-10 ppm

Table 8-II (Continued)

	Infrared spectrophotometry	Colorimetry	Electrical conductivity	Halogen leak-detector
Hydrocarbons	0-1000 ppm			
Oxygen containing organics	1-1000 ppm	0-100 ppm		
Halogenated organics		0-100 ppm 100-500 ppm	0-10 ppm 10-1000 ppm	0-10 ppm 10-1000 ppm
Inorganic oxides	1-1000 ppm	0-100 ppm 100-1000 ppm	0-10 ppm 10-1000 ppm	
Odors				
Aromatic hydrocarbons	0-1000 ppm			
Polynuclear hydrocarbons				

Table 8-II (Continued)

	Emission spectrometer	Mass spectrometer	Scantometer
Hydrocarbons		0.5-100%	
Oxygen-containing organics		0.5-100%	
Halogenated organics	0-500 ppm	0.5-100%	
Inorganic oxides		0.5-100%	
Odors			1-1000 LTV
Aromatic hydrocarbons		0.5-100%	
Polynuclear hydrocarbons			

Either two similar cylinders and two resistances or four similar cylinders and resistances are used to form the arms of a Wheatstone bridge circuit. The final equilibrium temperature of the wire depends upon the thermal conductivity of the gas surrounding it. Lower temperatures produce higher conductivity, whereas higher temperatures produce lower conductivity. If the gases in the cells are the same, the wires will reach the same temperature and therefore will have the same resistance; thus the bridge is balanced. If the gases are different, the final temperatures and resistances of the wires will be unbalanced. The extent of unbalance of the bridge is measured by a galvanometer or a potentiometer and can be calibrated in terms of the composition of the gas.

The thermal conductivity method is usually operated as a continuous recording method, since the off balance condition can be measured by a recording potentiometer.

The method is easily applied to the determination of the composition of binary mixtures, provided that the two gases have different thermal conductances (Willard, 1958). The greater the difference between the two gases, the greater the sensitivity of the method. A multicomponent mixture can be treated as a binary mixture if all components but one remain constant or if all the gases except one have nearly the same thermal conductance (Eckman, 1950).

With multicomponent mixtures, the thermal conductivity detector is frequently used in conjunction with gas-liquid chromatography. The components are separated by a packed column with each component exhibiting a characteristic retention time. Quantitative measurements are made by comparing peak heights or areas against standards.

Catalytic Combustion - The measurement of combustible gases or vapors is based on the principle of catalytic combustion (Mine Safety Catalog No. 8B3659-3, 1971). A mixture of gases may be either flammable or not, according to the concentration of the vapor in air in which a flash will occur or a flame will travel if the mixture is ignited. The lowest percent at which this occurs is the lower explosive limit (LEL) and the highest percent is the upper explosive limit (UEL). The LEL is considered 100% and the concentration below are considered as percent of the LEL.

If propane and air are confined and ignited, an explosion results. The LEL of propane in air is 2.2% and the UEL is 7.3%. Mixtures above 7.3% are too rich to support combustion, and those less than 2.2% are too lean. Since air is the diluent and is readily obtainable, all concentrations above 2.2% are dangerous; therefore the instrument would be calibrated from 0 to the 2.2% LEL for propane.

The catalyst is usually a platinum wire filament (Mine Safety, 1971 and Scott Aviation, 1969) maintained at a constant temperature. When the combustible gases or vapors come in contact with the catalytic filament, they are oxidized or burned catalytically. Two identical filaments are used in the bridge circuit. One filament, known as a reference filament, is sealed in air in a separate well of the same chamber as the active or exposed filament. Two fixed resistors are used as the legs of the bridge connected together by a variable resistor. The bridge is balanced with both filaments in air by adjusting the variable resistor or zero control. The increase in resistance is proportional to the amount of flammable gases or vapors in the sample and is measured by a meter, the scale of which is calibrated to give direct readings in percent of the LEL.

Portable combustible gas indicators may sample automatically or manually for the detection of combustible toxic gases or vapors. The ranges and sensitivities of the indicators depend on the model and the gases or vapors for which the instrument is calibrated. The instrument may operate on one full scale, a dual scale, or as high as five scale ranges which may read 0 to 1.0%, 0 to 10% or 0 to 100% of the lower explosive limit. For the gases or vapors calibrated for those indicators with two or more scales, ranges can be provided with multiple calibrations, whereby readings on any gas or gases for which it has been calibrated can be made by turning a selector switch. There are more sensitive models that read 0 to 1.0% of the lower explosive level on one scale and 0 to 1,000 ppm of vapor on a second scale (Johnson-Williams Products, 1970). Other models, while not scaled off in ppm designation, may be calibrated to measure in this low level area. These models provide a check on the toxicity of combustible vapor concentrations and furnish ppm measurements for comparison with threshold value limits.

A partial listing of selected gases and vapors that are reported to be measurable by catalytic combustion devices in the ppm range are listed in Table 8-III (Johnson-Williams Products, 1970).

Continuous combustible gas detectors (General Monitors, 1970; Mine Safety, 1970; Erdco Engineering, 1970) consist of two components: the control and indicating unit and a remote detection unit. The control unit is individually powered

Table 8-III Partial Listing of Gases and Vapors Detectable in the ppm Range*

Acetone
Amyl acetate
Benzene
Butadiene
Butyl acetate

Butyl alcohol
Cyclohexane
Cyclohexanol
Cyclohexanone
Ethyl acetate

Ethyl alcohol
Ethylene
Ethyl ether
Formaldehyde
Heptane

Hexane
Methane
Methyl alcohol
Methyl butyl ketone
Methyl ethyl ketone

Methyl isobutyl ketone
Methyl propyl ketone
Octane
Pentane
Perchloroethylene

Propane
Isopropyl alcohol
Propyl alcohol
Stoddard solvent
Toluene

1,1,1-Trichloroethane
Trichloroethylene
Turpentine
Xylene

*Most aromatic hydrocarbons are reported to be measurable in the ppm range by sensitive combustible gas indicators.

and contains the indication and warning devices. The remote detection unit designed for area monitoring, houses the catalytic sensing device. Each control unit may be coupled with a single or a dual detection unit for monitoring locations as far as 3000 to 5000 ft away. Several control units may be housed in modules to facilitate centralized monitoring from multiple locations.

Combustible gas or vapor is detected at the sensory probe by means of a low temperature catalytic reaction on a heat sensitive surface. Matched elements are heated and exposed to the gas or vapor. One element in the pair is catalytically active; the other is inactive and acts as reference.

In the presence of a combustible gas, oxidation takes place on the active element, slightly raising its temperature. This increases the resistance of a leg of a circuit bridge and gives a direct current signal which drives the meter and accessory circuit. The gas concentration for which the unit is calibrated is displayed in percent of the LEL.

The assembled units offer continuous monitoring of areas in multiple locations. The units may be calibrated to give direct readouts of combustible gases and vapors in one or two ranges, 0% to 100% or 0% to 10% of the LEL. The continuous sensory filaments operate at about one-half the temperature of the conventional platinum wire filaments; therefore the life of the circuit bridge is relatively long. A bridge life of 10,000 hr in air has been reported. The control unit contains the alarm circuitry for indicating failure of the sensing device or an increase of vapor concentration, readout circuitry for powering the meter or potentiometric records, and all operating controls.

The assembled units are adaptable for use with any gas or vapor whose molecular weight and explosive range are known. Their application, therefore, extends to all industries where combustible fluids and resultant gases and vapors are employed.

Ionization - The flame ionization detector operates by burning hydrogen in air to produce a flame that contains a negligible amount of ions. When hydrocarbons are introduced into the hydrogen flame an ionization process ensues, whereby a large number of ions are produced. An electrostatic field in the vicinity of the flame causes an ion migration in which positive ions are attracted to a collector and the negative ions to a burner jet. The small ionization current established between the two electrodes is measured by an electrometer and the signal indicated by a meter or by a potentiometric recorder. The magnitude of the signal is an indication of the number of carbon-hydrogen bonds passing through the flame and this is directly proportional to the hydrocarbon concentration. The sampling system is an integral part of most commercial total hydrocarbon analyzers, designed to measure continuously total hydrocarbon and other organic compound concentrations in a gas stream or ambient air (Davis Instr. Div., 1965; Bendix, 1970; Beckman Instr., 1969).

Trace quantities of such organic compounds as hydrocarbons (aliphatic and aromatics), aldehydes, amines, ketones, acetates and alcohols in part-per-million range in air may be detected. Carbon atoms bound to oxygen, nitrogen, or halogens give reduced or no response, whereas there is no response to nitrogen, carbon monoxide, carbon dioxide or water vapors (EPA, 1971).

The analyzers are usually calibrated using methane and results recorded in terms of methane equivalents. A number of other gases such as butane and propane may also be used depending on the sensitivity desired and the type of organic to be monitored.

The specification for a given total hydrocarbon analyzer will vary as to model or manufacturer. They may be portable or used as a stationary unit adaptable to many industrial monitoring applications and as elaborate as the addition of optional support equipment. The instrument may offer one full scale range or 5 to 6 ranges with a 1:10 gain. The full scale range may be 0 to 1 ppm, 0 to 10 ppm or through several ranges up to 0 to 10,000 ppm hydrocarbons per calibration equivalent. The range may be varied by adjusting the attenuation and flow rate of the sample to the detector. Accuracies and noise levels are also different and are expressed in terms of percent of the lowest full scale per calibration gas. Zero drift varies and depends on airflow rate, sample flow rate, fuel flow rate, ambient temperature change, detector contamination and electronic drift. Zero drift is usually expressed in range percent/24 hour period.

Other recording instruments using an ionization principle for the determination of trace gases in the parts-per-million and in some cases in the parts-per-billion range have been developed and are commercially available (American Industrial, 1960).

This method of gas analysis uses an ionization chamber to detect an aerosol which is formed from the contaminant in a number of ways. The ionization chamber is composed of a stainless steel cylinder electrode and an inner electrode of a heavy wire. An alpha emitter is placed along the inner surface of the cylinder. The two electrodes are given opposite charges which cause a flow of ion current through the gas between them.

With only air present in the chamber, there is a relatively constant flow of ion current. However, very small concentrations of particular matter cause a pronounced drop in this flow of ion current. The effect of the particulates on the conductivity of the ion chamber is a measure of the concentration of the gas or vapor of interest (Mine Safety, 1970). The formation of particulates for a wide range of materials is accomplished by: reacting the trace gases with various reagents to produce particulate matter; direct pyrolysis of the sample; or a combination of both chemical reaction and pyrolysis.

The conductivity is measured by a detector cell and a compensator cell placed on two arms of a Wheatstone bridge circuit. The presence of particulates causes a drop in ion current in the cell and results in an unbalance of the bridge which is amplified for driving a meter or a recorder.

There are portable models that are reported to be accurate as well as easily operated. Applicable to the scope and nature of this survey are the analyses of acid and alkaline gases, oxides of nitrogen, and amines which are sensitized through reactions with specific reagents. For example, ammonia may be used to sensitize such materials as halide acids, nitric oxide and sulfur dioxide. A combination of pyrolysis and use of a reagent may be employed in the determination of organic halides. On passing a chlorinated hydrocarbon through a copper oxide converter at elevated temperatures, a copper chloride aerosol is formed.

The overall applicability of this instrument is limited as to the variety of gases and vapors it can monitor. Several of these gases have been mentioned, but its strongest asset is not variety but the sensitivity that the instrument can achieve.

Ultraviolet Spectrometry - Ultraviolet analysis measures the degree of light absorption as it occurs in a gas or liquid sample. The ultraviolet spectrum ranges from 100Å to 3800Å, and those gases whose nature it is to absorb in this ultraviolet region can be measured. In general, ethylene, carbonyl structures and molecules which include the benzene ring in their structure all absorb in the ultraviolet region (Holzbock, 1955 and American Industrial, 1960).

The ultraviolet spectrophotometer will detect gases and vapors at low concentrations and will detect a great array of gases and vapors that absorb in the ultraviolet band. The instrument may therefore be used either for complete analyses of samples by running a complete spectrogram, or for continuous analysis of process streams by operating at a fixed wavelength critical to the analysis being made (Eckman, 1950).

Ultraviolet spectrophotometry may be applied to the detection of trace amounts of benzene, toluene, and other aromatic hydrocarbons, and chlorinated solvents in air in the ppm range (Univ. of Michigan, 1956). Polynuclear aromatics, some of which are believed to be carcinogenic, have been qualitatively detected and quantitatively analyzed by ultraviolet spectrophotometric methods (American Industrial, 1960) and as previously mentioned, ethylene and carbonyl structures absorb in the ultraviolet band and are therefore detectable with this method.

Descriptions and illustrations of several types of ultraviolet spectrophotometers as well as other spectrophotometric instruments that are commercially available have been compiled (Willard, 1958). Special mechanisms have also been described which permit automatic measurement on as many as three plant streams by one instrument (Holzbock, 1955). Most spectrophotometers are for stationary use as opposed to the more portable photometers.

Infrared Spectrometry - The infrared spectrum ranges from wavelengths of 7800Å to 3,000,000Å. Those gases or vapors which will absorb in this heat radiation band can therefore be measured. This applies to the analysis of almost any organic and some inorganic compounds under the proper circumstances (American Industrial, 1960).

Of all molecular spectroscopy, the infrared spectrophotometer is the most versatile. Infrared spectrophotometers may be used to analyze an entire sample or at least a number of its constituents. However, there are other infrared spectrophotometers that are designed to continuously analyze for one constituent in a given sample. These instruments may be used to analyze in the ppm range such compounds as carbon monoxide, carbon dioxide, ethylene, isobutane and other substances that have infrared absorption characteristics. Conversely, elemental diatomic gases like oxygen, hydrogen, nitrogen, helium, chlorine, etc do not have absorption characteristics. Within acceptable substances the concentration of any component in a mixture can be determined by the specific absorption pattern that is unique for each component.

There are three basic types of infrared spectrophotometers: the dispersion analyzer, the positive nondispersion analyzer and the negative nondispersion analyzer (Holzbock, 1955). Common to all three types are: they have been employed in commercially available instruments; they provide continuous measurement; and they analyze for only one constituent either alone or in mixture for concentrations as low as ppm.

The dispersion analyzer concentrates upon a single wavelength or a narrow wavelength band within the infrared spectrum. The radiation of a particular wavelength that passes through the sample without being absorbed is measured. Generally, light of a second wavelength is simultaneously applied and the ratio of transmission at two wavelengths is measured. The dispersion analyzer may be readily adjusted for various wavelengths and maximum sensitivity. However, the optical system may become relatively complex.

Unlike the dispersion analyzer, the two nondispersion analyzers utilize all the energy from an infrared radiation source and pass it through the sample, unless the width of the wavelength band is limited by filters. In addition, the nondispersive analyzer usually splits the infrared radiation into two parallel beams.

The positive nondispersive analyzer operates by passing one beam through the sample to be analyzed and from there into a cell which is filled with the component to be detected. The other beam passes directly to a second cell with the same component. The gas in both cells expands due to the heat absorbed from the infrared radiation. The cell directly exposed to the infrared radiation will expand more than the cell which received infrared radiation only after it had passed through the sample. The relative expansion of the two cells is then usually measured by means of a variable capacitor. Also characteristic of this analyzer is a light chopper that interrupts the radiation of the infrared light source periodically, largely eliminating the effect of changing ambient temperatures.

In the negative nondispersion analyzer, both beams pass through the sample, but one traverses an additional cell which is filled with the component to be detected. The nonabsorbed radiation from each beam is then measured by a thermocouple or bolometer and the difference measured as an indication of the concentration of the component for which the sample is analyzed. This analyzer is characterized as being more sensitive to ambient temperature than the positive type, less sensitive as an analytical instrument but simpler and more rugged.

The prisms for the infrared spectrophotometers are usually made of four materials. The prism materials include lithium fluoride, calcium fluoride, sodium chloride and potassium bromide but quartz and cesium bromide have also been used (Willard, 1958 and Eckman, 1950). The selection of the prism is determined by the wavelength range most adaptable to the substance under analysis.

These infrared spectrophotometers have been described as being reliable and easily maintained. They are relatively rugged and yet versatile; they are simple in design, yet possess wide construction tolerance (Conn, 1960).

Colorimetric - Colorimetric methods include general laboratory wet chemical techniques as well as direct reading colorimetric instrumentation. The principle is based on the formation of a specific color resulting from the reaction of the contaminant with reagent or number of reagents. The resultant color is then measured with a photometer. Sensitive and specific colorimetric reactors have been developed for many of the air pollutants. Methods of colorimetric analysis are divided into three basic classes:

1. Detector tubes
2. Laboratory methods
3. Automatic instruments

The initial cost investment and the degree of technical skill required for application of these methods are represented in increasing order.

Detector tubes provide a noninstrumental technique for semiquantitative analyses for many toxic gases and vapors in the threshold limit ranges. The detector tubes are glass tubes which contain selective, reactive chemicals impregnated on sands, alumina gels, silica gels or other gels. The composition of the reactive substrate is determined by the gas or vapor to be tested. As an example, for hydrogen sulfide, the substrate may consist of granular silver cyanide on activated alumina. For sulfur dioxide a mixture of iodine gel and tetrabase sand may be used. A yellow silica gel impregnated with a complex silico-molybdate compound catalyzed by palladium sulfate is used for carbon monoxide. For aromatic hydrocarbons, the substrate used may be a mixture of sulphuric acid gel and paraformaldehyde sand (Univ. of Michigan, 1956).

Samples of the contaminated air are drawn through the tubes by means of aspirators or assorted hand pumps. Some hand pumps provide for measured volume samples, while both aspirators and hand pumps are equipped with variable orifices. The measured sample is drawn through the substrate and the gas or vapor reacts with the chemicals in the substrate, producing a stain which is directly proportional to the concentration of that gas or vapor in the suspected stream. The length of the stain is measured by an appropriate precalibrated scale for the vapor being tested. The stain may develop directly with contact of the gas or vapor or may be developed with the addition of reagents.

The detector tubes are usually supplied as kits, with aspirators or hand pumps provided. A listing of the gases and vapors for which the detector tubes can be used are provided by the manufacturers (Davis Instr. Div., 1963 and Mine Safety, 1971). Also included in this listing are those compounds that interfere with the respective reaction. The effect of the interference should therefore be considered when measuring for specific compounds. Necessary reagents are also provided when applicable. The detector tubes may be the ready-to-use type or those that are mixed prior to use and equipped with special filters and prefilters. Remote sampling kits are available for sampling inaccessible areas. In addition to these accessories, a pyrolyzing unit may also be provided. The pyrolyzer separates toxic compounds by the application of heat, whereby specific chemicals are released whose concentration can be related to the level of the original compound.

This type of detection is particularly suitable for the small businessman. The initial cost is quite low, the technical skills required to analyze a sample are practically nil and small businesses generally emit a single pollutant.

Laboratory colorimetric methods require a photometer for measurement of the concentration of a developed color. Photometers vary in complexity and concomitant cost. Simple photometers employ a light source, filters, phototube and readout. The more complex and expensive photometers use gratings or prisms to provide light of the desired wavelength. The sample which is collected must be treated chemically to remove interferring contaminants, if present, and develop the desired colored compound. This, of course, requires some technical skill plus associated laboratory apparatus.

Automatic colorimetric instrumentation is available for many contaminants. The basic instrument consists of a sampling pump, a scrubber system to remove the contaminant from the gas stream, automatic liquid metering of the solution, automatic reactant feed, associated electronics and controls and direct readout. The instrument is versatile in that various contaminants can be analyzed by changing the scrubbing solution or reactant. This type of instrument generally requires a high degree of technical skill to select the appropriate separation and reactant solutions and to maintain the instrument in a reliable operating condition.

Electroconductivity - The electroconductivity analyzer continuously records concentrations of gases or vapors that will ionize in water either directly or after decomposition by heat. The principle of measurement is the differential measurement of conductivity before and after a gas sample ionizes in distilled water. The conductivity is measured by two sets of platinum electrodes arranged in an alternating current bridge circuit. This type of instrument is usually used to continuously record atmospheric concentrations, but has been adapted for process control (Univ. of Michigan, 1956). Instruments are available which permit periodic check of gases or vapors at 3 to 13 remote points and the results are shown on various recorders (Univ. of Michigan, 1956).

A continuous flow of water scrubs the gas sample stream. The mixture is circulated around the platinum electrodes and the amount of ionization is indicated. The water is then passed through a deionizing bed and recirculated through the system. In some instances the sample need not pass through the pyrolyzing furnace before scrubbing with the water.

This type of system makes for a basic analyzer and is adapted for the measurement of one gas or vapor in air in the ranges of 1 to 5 ppm or lower if necessary for such vapors as chlorine, sulfur dioxide and hydrogen sulfide (American Industrial, 1960). Carbon tetrachloride, and the oxides of nitrogen may also be determined. The system may also be employed for the determination of organic chloride vapors (Davis Instr. Div., 1963 and American Industrial, 1971).

Halogen Leak Detection - Halogen leak detectors maintain an ion current by electrically exciting an emitter. The detector sensing element for the halogen leak detector is a diode consisting of a heater element (positive) and a collector (negative) arranged coaxially (General Electric).

A positive ion current flows at all times from the emitter to the collector. When a trace of halogen gas is present between the collector and emitter the ion current increases markedly. The increase in ion current is linearly proportional to the concentration of halogen from 0 to 1 ppm. For concentrations from 1 ppm to about 1000 ppm, the increase is exponentially proportional. Above 1000 ppm, no further increase of ion current occurs and the element desensitizes rapidly but cleaning usually restores original sensitivity.

These instruments are portable and are designed for continuous operation. The instruments are nonspecific in the determination of halogenated hydrocarbons or mixtures of halogenated hydrocarbons. Nonhalogenated compounds such as hydrocarbons, will not interfere, however; and mixtures of halogenated vapors with other vapors may be measured.

Designed for field use, the normal operating range is 0 to 500 ppm for most substances. The lower limit of detection is about 10 ppm and the accuracy throughout most of its range is about 10% of the amount being measured. The instruments employing this principle are most often used for the determination of perchloroethylene, trichloroethylene, carbon tetrachloride, methylene chloride and other similar halogenated hydrocarbons (Univ. of Michigan, 1956 and Davis Instr. Div., 1971).

Emission Spectrometry - Emission spectrometers are usually employed in the determination of elements and metallic compounds. However, this principle has been applied to the determination of halogenated hydrocarbons in air (Davis Instr. Div., 1971). Briefly, emission spectrometers employ an arc spark for producing radiation emissions and a grating for refracting emitted radiation into a spectrum. The intensity of the radiation lines are measured directly by means of phototubes.

In this particular type of spectrometer, air containing halogenated hydrocarbons is passed through a chamber containing an alternating current electric arc between a copper electrode and a platinum electrode (Univ. of Michigan, 1956). A bright line spectrum of copper is produced when the air surrounding the arc contains halide vapors. The intensity of the copper spectrum is proportional to the concentration of halide vapors present, and the blue lines are measured with a blue sensitive phototube fitted with a blue glass filter. The change in current output of the phototube is then measured by a direct current vacuum tube voltmeter.

This type of instrument is expensive and is expected to have little application in the measurement of absorbent bed inlet and outlet concentrations.

Mass Spectrometry - The mass spectrometer separates ions of various atoms, molecules or their fragments by passing the ions of these materials through a magnetic field. The ions are deflected according to their mass and charge and impinge upon a collector. The current intensity of the collector is proportional to the number of ions which impinge on the collector.

Mass spectrometers are highly specific for individual contaminants. The disadvantages are that they do not possess the low level sensitivity of many other instruments, they are expensive and they are not portable. Sensitivity can be increased by concentration of a specific impurity of interest. Mass spectrometers are amenable to analysis of high concentration of contaminants and the results from this type of analysis can be used to determine what type of sorbent bed should be used, to size the bed, and to predict the life time of the bed.

Scentometry - Measurement of odors is, at best, semiquantitative even when only a single odiferous material is present. When the test atmosphere contains a mixture of odiferous materials, even semiquantitative identification is essentially impossible. Fortunately, many processes emit only one odor and since package sorbent devices will be used in many cases for odor control, it will be a straightforward task to determine when the device needs replacement or regeneration.

A scentometer is marketed which provides a means of multiple dilution of a sample. A trained panel smells each diluted sample and, if the pollutant is known, an estimation can be made of its concentration.

Another method of quantitatively defining odors is given in ASTM D 1391-57. A sample is collected in an air sampling syringe. The contents of the air sampling syringe is then injected into a mixing syringe and diluted with 100 ml of clean air. After 15 sec, the syringe is placed near the nostrils and the content is ejected for 2 to 3 sec. Various dilutions are made until the odor is just perceptible. The ratio of the total volume of the diluted sample to the volume of the original sample in the diluted sample is a measure of the concentration of odor in the original sample. Table 2-IV lists the odor threshold of some air pollutants.

Recommended Methods for Specific Classes of Impurities

Hydrocarbons

The hydrocarbons can be measured as a general class by flame ionization detection down to the ppm level. Gas-liquid chromatography can be used to separate the various hydrocarbons and, when used in conjunction with flame ionization detection, individual hydrocarbons in a hydrocarbon mixture can be measured at the ppm range. Ultraviolet and infrared spectrophotometry can be used to measure individual hydrocarbons in low ppm ranges, also. Catalytic combustion provides a means of detection at low levels, but is generally applicable only when a single hydrocarbon (and no other catalytically combustible material) is present. Thermal conductivity is applicable down to about the 100 ppm level and can be used in conjunction with gas-liquid chromatography for the detection of specific hydrocarbons. Mass spectrometry is limited to measurement at approximately the 0.5% level but does provide detection of the individual hydrocarbons.

Oxygen Containing Organic Compounds

These compounds exhibit essentially the same detection characteristics as the straight chain hydrocarbons. Again, flame ionization is the most sensitive means of detecting this class of compounds and chromatography can be used to separate the various oxygen containing organics. Sensitivity colorimetric methods have been developed for measurement of oxygen containing organics, also.

Halogenated Compounds

The halogenated compounds are particularly sensitive to electron capture detection. The electron capture detector has been used in conjunction with gas-liquid chromatography to separate and detect mixtures of halogenated compounds. The halogen leak detector is a suitable instrument for the detection and measurement of halogenated compounds, also. The flame ionization detector can be used if a single halogenated hydrocarbon is being detected.

Inorganic Oxides

Oxides such as CO can be measured by catalytic combustion down to the few ppm level. Sensitive chemical methods are available for the detection of other inorganic oxides such as SO_2; instrumentation has been developed which will automatically perform this function.

Odors

They pose the greatest problem in terms of quantification. Fortunately, olfactory detection is the most practical means of sensing odors and, since the objective of sorbent systems is to remove these odors, an inexpensive means of detection exists. Semiquantitative estimations can be made with the use of a scentometer.

Aromatic Hydrocarbons

These can be detected by the same methods used for measurement of straight chain hydrocarbons. Again, flame ionization detection provides the most sensitive means of detection. Sensitive colorometric methods have been developed for many of the aromatics. Other methods include ultraviolet and infrared spectrophotometry.

Polynuclear Hydrocarbons

The polynuclear hydrocarbons are generally of interest in the low ppm to ppb range due to the carcinogenic nature of many of these compounds. Because of this low level requirement and since other hydrocarbons are generally present with the polynuclear hydrocarbons, ultraviolet or infrared spectrometry are the best means of measuring this class of compounds. Colorimetric methods are also applicable in certain cases.

Appendices

A	Glossary
B	Information Sources
C	Tables of Data
D	Methods
E	Sample Calculations
F	Literature Cited
G	Bibliography

Appendix A

Glossary

A	Adsorption potential equal to $[T/V_m] \log [p_o/p]$, also a constant
A_c	Area of adsorbent or catalyst bed, also collision coefficient
B	Constant
C	Pollutant vapor concentration, also a constant
C_b	Pollutant breakpoint effluent concentration
C_e	Pollutant effluent concentration from adsorbent or catalyst bed
C_i	Pollutant influent concentration to adsorbent or catalyst bed
C_o	Concentration of saturated vapor
D	Diameter of adsorbent or catalyst bed
D_p	Adsorbent or catalyst particle diameter
D_v	Diffusion coefficient
E	Heat of adsorption on different layers, also kinetic energy
F	Total gas flow
ΔF	Free energy change equal to $-RT \ln [p_o/p]$
ΔH	Heat of adsorption or desorption
K	Reaction rate constants
K_f	Volumetric film heat transfer coefficient
L	Adsorbent or catalyst bed length or depth measure
L_c	Critical bed length
L_s	Saturated bed length
L_t	Total bed length
L_z	Adsorption zone length
M	Molecular weight
N	Avogadro's number, 6.03×10^{23} molecules/mol
P, P_A	Total pressure
ΔP	Pressure drop through adsorbent or catalyst bed
Q	Heat of reaction, total heat
R	Gas constant
S	Surface area
ΔS	Entropy change
T	Absolute temperature
U	Face velocity to adsorbent or catalyst bed
U_m	Intergranular gas velocity in adsorbent bed

V	Liquid molar volume of pollutant vapor at ambient temperature
V_m	Liquid molar volume of pollutant vapor at normal boiling point
V_c	Catalyst or adsorbent bed volume
W	Total weight, adsorbent, catalyst or pollutant
W_c	Weight of carbon
W_r	Total weight of pollutant remaining in carbon after regeneration
W_s	Total weight of pollutant adsorbed in carbon saturated layer
W_z	Total weight of pollutant adsorbed in carbon adsorption zone
a	Superficial area of particles per unit volume of particles
a,b,c	Component species
d	Pore diameter, carbon density
h	Planck's constant, Wheeler mechanism index
k	Constant
n	Number of adsorbed layers, constant in Freundlich equation
p	Pollutant vapor pressure
p_o	Vapor pressure of pure liquid
r	Pore radius
t	Time, service time
t_b	Service time to breakthrough concentration of C_b
t_c	Contact time
v	Volume of adsorbed vapor
v_m	Volume of vapor required to form a unimolecular layer
α	Polarizability
α,β,γ	Constants
γ	Surface tension
ε	Void volume in adsorbent bed
ε_i	Polanyi potential
η	Viscosity
θ	Fraction of surface area covered
λ	Heat of vaporization of pure liquid
μ	Dipole moment, viscosity of pollutant in air
ν	Characteristic light dispersion frequency
ρ	Gas density
σ	Distance between centers of two dipoles
τ	Multilayer correction factor
ϕ	Contact angle
ω	Amount pollutant adsorbed per unit quantity of adsorbent

ω_r	Mean amount of pollutant adsorbed per unit quantity of adsorbent that remains at the end of regeneration
ω_s	Amount pollutant adsorbed in saturated layer per unit quantity of adsorbent
ω_z	Mean amount pollutant adsorbed in adsorption zone per unit quantity of adsorbent

Appendix B

Information Sources on Air Pollution

Trade Associations in the Washington, D.C. Area

Bureau of Raw Materials for Vegetable Oil & Fats
Council of Independent Laboratories
National Drycleaners Institute
National Paint, Varnish & Lacquer Association
Manufacturing Chemists Association
National Fisheries Institute
Bureau of Fish Oil and Meal Processes
Research Council of the Graphic Arts Institute

Trade Associations in the Chicago Area

National Restaurant Association
Brewers Association
Institute of Baking
National Canners - NCA Staff Center
Candy & Confectioners Institute
National Renderers Association
American Meat Institute
Institute of Paper Chemistry

Pollution Control Agencies

Allegheny County Dept. of Health
Pittsburgh, Pennsylvania

Southwest Air Pollution Control Authority
Vancouver, Washington

Los Angeles County Air Pollution Control District
Los Angeles, California

District of Columbia Dept. of Public Health
Washington, D.C.

Bureau of Air Pollution Control
Illinois Dept. of Public Health
Springfield, Illinois

Wyoming Dept. of Public Health
Cheyenne, Wyoming

Bay Area Air Pollution Control District
San Francisco, California

Environmental Control Board
New York, New York

Houston Health Department
Houston, Texas

Fulton County Health Department
Atlanta, Georgia

Albuquerque Dept. of Environmental Health
Albuquerque, New Mexico

Air and Water Pollution Control
City of Jacksonville
Jacksonville, Florida

City of Chicago Dept. of Air Pollution Control
Chicago, Illinois

Dept. of Public Health
Philadelphia, Pennsylvania

Denver Air Pollution Control Agency
Denver, Colorado

Division of Air Pollution Control
St. Louis, Missouri

Plant Trips, Pollution Control

Vic Manufacturing Company
Minneapolis, Minn.

American Machinery and Foundry
Minneapolis, Minn.

Vulcan Cincinnati, Inc.
Cincinnati, Ohio

Charleston Rubber Co.
Charleston, South Carolina

Reigel Paper Co.
Edenburg, Indiana

Norfolk Tallow Co.
Chesapeake, Virginia

Government Documents

Title	Wash. D.C. Ident. No.
Atmospheric Emissions from Fuel Oil Comb.	AP-2
A Pilot Study of Air Pollution in Jacksonville, Fla.	AP-3
Air Pollution and the Kraft Pulping Industry	AP-4
Dynamic Irradiation Chamber Tests of Automotive Exhaust	AP-5
Air Pollution in the Coffee Roasting Industry	AP-9
Community Perception of Air Quality	AP-10
Reactivity of Organic Substances in Atmospheric Photooxidation	AP-14
Selected Methods for the Measurement of Air Pollution	AP-11
An Air Pollution Management Plan for Nashville	AP-18
Effects of the Ratio of Hydrocarbon to Oxides of Nitrogen, Auto Exhaust	AP-20
Continuous Air Monitoring Program, Cincinnati	AP-21
Continuous Air Monitoring Program, Washington,DC	AP-23
Atmospheric Emissions from Coal Comb.	AP-24
Seminar on Human Biometeorology	AP-25
Workbook of Atmospheric Dispersion Est.	AP-26
Air Pollution Aspect of Tepee Burners	AP-28
Rapid Survey Technique for Estimating Community Air Pollution Emissions	AP-29
Selection and Training of Judges for Sensory Evaluation Diesel Exhaust Fume	AP-32
Sources of Polynuclear Hydrocarbons in the Atmosphere	AP-33
Air Pollution Engineering Manual	AP-40
Compilation of Air Pollutant Emission Factors	AP-42
A Compilation of Selected Air Pollution Emission Control Regulations and Ordinances	AP-43
Handbook of Air Pollution	AP-44
Interim Guide of Good Practices for Incineration at Federal Facilities	AP-46
Air Pollution Translations, Vol. I	AP-56
Air Quality Criteria for Carbon Monoxide	AP-62
Air Quality Criteria for Hydrocarbons	AP-64
Air Pollution Translations, Vol. II	AP-69
National Survey of the Odor Problem, Phase I, Jan. 1970, prepared by Copley Int. Corp.	
Nationwide Inventory of Air Pollutant Emissions, 1968, HEW	

SURVEY OF AIR POLLUTION FROM SMALL STATIONARY SOURCES

AN AIR POLLUTION CONTROL AGENCY REPORT

Section I General Information

Name of agency: ______________________________

Address: City__________ State_________ Zip____

Name of individual: ___________________________

Title: ______________________________________

Telephone number: AC___/_________

Date: ___________________________

Responsible for pollution control in: (name)

Township _______________________

City __________________________

County ________________________

State _________________________

Region ________________________

Responsible for emission from: (check)

Commercial ☐

Industrial ☐

Agricultural ☐

Institutional ☐

Section II Emissions Source Complaints

The purpose of this question is to determine the need for control of the various small emissions sources.

Fill in appropriate square with number of complaints per year. If complainants did not identify odor or other effect produced by an air pollutant emitted by a source, these may be recorded in the last column. The next to last column, ill-effect on health, refers to headaches, nose, lung or skin irritations.

	Number of complaints per year									
	Sulfurous odor	Petroleum odor	Solvent odor	Food odor	Burning odor	Decay odor	Effect on vegetation	Corrosion	Ill-effect on health	Unidentified
Dry cleaning	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
Paint shop	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
Print shop	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
Electroplating shop	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
Gasoline transfer	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
Restaurants	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
Food stores, markets	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
Small chem. mfg.	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
Incinerators, dwelling, school, hospital	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
Others										
______________	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
______________	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
______________	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐
______________	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

Section III Amount of Air Pollutant Discharged From Small Emission Sources

The purpose of this question is to determine the problems that might be encountered in the control of emissions by package sorbent or catalytic combustion devices. It also supplies information on sizing of the control devices for the various pollutant producing operations.

The following table has four column headings under which data may be tabulated.

Size of source asks for a judgment as to the medium size or size range for each operation in terms used by the particular trade.

Type, odor or chemical formula asks for identification of the pollutant in terms of type of odor, or chemical formula or class of compounds (halogen, sulfurated, hydrocarbons) with some estimate of molecular weight range.

Rate of emission asks for data on amount of pollutant lost to the atmosphere per unit of time, or per unit of material processed or per unit serviced.

Concentration and/or rate of air exhaust asks for data on pollutant concentration with air exhaust rate if data on rate for previous column is not on record. In the case of odor, total air exhaust rate may be the only numerical information available for the last two columns. Exhaust rate should be identified with size of source.

Source	Size of source	Type, odor or chemical formula	Rate of emission	Conc. and/or rate of air exhaust
Dry cleaning				
Paint shop				
Print shop				
Electroplating shop				
Gasoline transfer				
Restaurants, etc.				
Food stores, markets				
Small chemical manufacturers				
Incinerators, dwellings, schools, hospitals				
Others				

Appendix C

Tables of Data

Table C-I Properties of Pollutant Vapors Emitted From Small Stationary Sources

Pollutant*	Chemical formula	V_m, cm^3/mol	Boiling point, °F	LEL, ppm	Industry number
Tridecanol	$CH_3[CH_2]_{12}OH$	305		---	4
Dodecane	$CH_3[CH_2]_{10}CH_3$	274	421	6,000	1
Undecane	$CH_3[CH_2]_9CH_3$	251	383		1
2-Ethyl hexyl acetate	$CH_3COOCH_2CH[C_2H_5]$-C_4H_9	238	390		5,8
Decane	$CH_3[CH_2]_8CH_3$	229	345	8,000	1,4,5
Butyl carbitol	$CH_3[CH_2]_3O[CH_2]_2$-$O[CH_2]_2OH$	213	448		1
Nonane	$CH_3[CH_2]_7CH_3$	207	302	7,400	1
2,6-Dimethyl-4-heptanone	$[(CH_3)_2CH\ CH_2]_2CO$	207	334	---	1,4,5,8
Nonanal	$CH_3[CH_2]_7CHO$	207	365		51
Diethyl cyclohexane	$[C_6H_{10}][C_2H_5]_2$	207			1
Butyl cyclohexane	$[C_6H_{11}]C_4H_9$	207	354		1
1,8-Octanediol	$HO[CH_2]_8OH$	203			4
4,5-Octanediol	$C_3H_7CH[OH]CH[OH]$-C_3H_7	203			4
Hexyl acetate	$CH_3COOC_6H_3$	196	336	---	4
2-Methyl pentyl acetate	$CH_3COOC_2H_3[CH_3]C_3H_7$	196			4
1-Octanol	$CH_3[CH_2]_7OH$	194	381	---	4
2-Octanol	$C_2H_4[OH][CH_2]_5CH_3$	194		---	4
1-Methyl pentyl acetate	$CH_3COOCH[CH_3]C_4H_9$	194			1,4

* Wherever possible the nomenclature approved by the International Union of Chemistry was used.

Table C-I (continued)

Pollutant	Chemical formula	V_m, cm³/mol	Boiling point, °F	LEL, ppm	Industry number
2-Ethyl hexanol	$C_4H_9CH[C_2H_5]CH_2OH$	194	365	---	4
Diethyl cyclopentane	$C_5H_8[C_2H_5]_2$	192	307		1
2,6-Dimethyl-2,5-heptadien-4-one	$[(CH_3)_2C = CH]_2CO$	192		8,000	4,7
Butyl cyclopentane	$C_5H_9[CH_2]_3CH_3$	188	314		1
Octane	$CH_3(CH_2)_6CH_3$	185	257	10,000	1,4,6,10,51
3-Octanone	$CH_3CH_2CO[CH_2]_4CH_3$	185		---	4
Octanal	$CH_3[CH_2]_6CHO$	185	336	---	51
Butyl benzene	$C_6H_5(CH_2)_3CH_3$	185	361		1
αPinene (turpentine)	$C_{10}H_{16}$	184	300	7,000	1,4
Butyl-2-hydroxy-propanate	$CH_3CH[OH]COOC_4H_9$	183			1,4
Pentyl acetate	$CH_3COO[CH_2]_4CH_3$	174	300	10,000	1,4,7
Carbitol	$CH_3CH_2O[CH_2]_2O$- $[CH_2]_2OH$	169	393	12,000	1
Phenyl acetate	$CH_3COO\ C_6H_5$	166	385	17,000	4
Dipropyl sulfide	$[C_3H_7]_2S$	166	ca 287		51
Difurfuryl ether	$[\underbrace{OCH = [CH]_2 = C}CH_2]_2O$	164	213		51
Heptane	$CH_3[CH_2]_5CH_3$	163	208	12,000	1,4,5,6,7,9
Heptanal	$CH_3[CH_2]_5CHO$	163	311		51
3-Heptanone	$CH_3CH_2CO[CH_2]_3CH_3$	163	302	---	4,5,8
5-Methyl-2-hexanone	$CH_3CO\ C_3H_5[CH_3]_2$	163		---	4
2,4-Dimethyl-3-pentanone	$[(CH_3)_2CH]_2CO$	163	255		7
Ethyl cyclohexane	$C_6H_{11}C_2H_5$	162	269		1

Table C-I (continued)

Pollutant	Chemical formula	V_m, cm^3/mol	Boiling point, °F	LEL, ppm	Industry number
Isopropyl benzene	$C_6H_5CH[CH_3]_2$	162	306	9,000	1,10
Propyl benzene	$C_6H_5[CH_2]_2CH_3$	162	318	8,000	1
Dimethyl cyclohexane	$C_6H_{10}[CH_3]_2$	162	ca 246		1
2-Phenoxy-ethanol	$C_6H_5O[CH_2]_2OH$	160		---	4
2-Butoxy-ethanol	$CH_3[CH_2]_3O[CH_2]_2OH$	160	ca 340	11,000	1,4
2-Ethoxy-ethyl acetate	$CH_3COO[CH_2]_2OC_2H_5$	160	313	12,000	1,4,5,8
1,6-Hexanediol	$HO[CH_2]_6OH$	159	482	---	4
2,3-Hexanediol	$C_3H_7[CHOH]_2CH_3$	159	402	---	4
Triethylamine	$[C_2H_5]_3N$	159	192	12,000	51,52
1-Methyl-propyl acetate	$CH_3COOCH[CH_3]\ C_2H_5$	155			1
Cyclooctane	C_8H_{16}	154	ca 298		4,5
Butyl acetate	$CH_3COOC_4H_9$	152	260	14,000	1,4,7
2-Methyl-propyl acetate	$CH_3COOC_2H_3[CH_3]_2$	155		---	1,4
Diisopropyl ether	$[(CH_3)_2CH]_2O$	152	ca 156	14,000	1,4
Isopropyl propyl ether	$[CH_3]_2CHO[CH_2]_2CH_3$	151	181		5,8
4-Methyl-2-pentanol	$[CH_3]_2C_3H_4[OH]CH_3$	150	266	10,000	1,4
2-Methyl-1-pentanol	$C_3H_7CH[CH_3]CH_2OH$	150	ca 298	---	4
4-Hydroxy-4-methyl-2-pentanone	$[CH_3]_2C[OH]-CH_2COCH_3$	150		18,000	4,7
2,4-Dimethyl-1,3-pentadiene	$CH_2=C[CH_3]CH=C[CH_3]_2$	148			51
2,3-Dimethyl-1,3-pentadiene	$CH_2=C[CH_3]C[CH_3]=C_2H_4$	148			51

Table C-I (continued)

Pollutant	Chemical formula	V_m, cm^3/mol	Boiling point, °F	LEL, ppm	Industry number
Dimethyl cyclopentane	$C_5H_8[CH_3]_2$	144			1
Ethyl cyclopentane	$C_5H_9[C_2H_5]$	144	217		1
2-Hexanone	$CH_3CO[CH_2]_3CH_3$	141	258	12,000	1
Hexanal	$CH_3[CH_2]_4CHO$	141	263	---	51
4-Methyl-2-pentanone	$[CH_3]_2CHCH_2COCH_3$	141	242	14,000	1,4,5,6,7,8
Pentachloroethane	$Cl_3C\ CHCl_2$	141	324	---	6
Xylene	$C_6H_4[CH_3]_2$	140	291	10,000	1,4,5,6,7,8
Ethyl benzene	$C_6H_5C_2H_5$	140	277	10,000	1
Hexane	$CH_3[CH_2]_4CH_3$	140	154	12,000	1,4,6,7,9,10,51
Asparagine	$H_2NCOCH_2CH[NH_2]$-$COOH$	140	415		57
Cycloheptane	$\underbrace{CH_2[CH_2]_5CH_2}$	137	244		4,5
2-Hydroxy-ethyl propanate	$C_2H_5COO[CH_2]_2OH$	137		15,000	4
αChlorotoluene	$C_6H_5CH_2Cl$	136	354		7
3-Methyl butanoic acid	$[CH_3]_2[CH_2]_2COOH$	134	350	---	51
4-Methyl-3-penten-2-one	$[CH_3]_2C{=}CHCOCH_3$	133	266	---	1,4
1,2-Dichlorobenzene	$C_6H_4Cl_2$	132	354	20,000	4,7,51
Propyl acetate	$CH_3COOC_3H_7$	129	214	20,000	1,4
Isopropyl acetate	$CH_3COOCH[CH_3]_2$	129	199	18,000	1,4
Cyclohexanol	$C_6H_{11}OH$	127	321	---	1,4
2-Methyl-2-butanol	$C_2H_5C[OH][CH_3]_2$	127	215	10,000	4
2-Pentanol	$CH_3[CH_2]_2CH[OH]CH_3$	127	246	12,000	4
1-Pentanol	$CH_3[CH_2]_4OH$	127	ca 279	10,000	1,4,51

Table C-I (continued)

Pollutant	Chemical formula	V_m, cm^3/mol	Boiling point, °F	LEL, ppm	Industry number
1,1,2-Trichloro-1,2,2-trifluoroethane	FCl_2CCClF_2	120	118	---	2,3
Pentane	$CH_3[CH_2]_3CH_3$	118	97	14,000	4,6,10,51
2-Pentanone	$CH_3[CH_2]_2CO\ CH_3$	118	215	16,000	1,4
Cyclohexanone	$C_6H_{10}O$	118	312	11,000	1,4,6,7
Toluene	$C_6H_5CH_3$	118	231	14,000	1,4,5,6,7,8,51
3-Methyl butanal	$[CH_3]_2CHCH_2CH\ O$	118	198	25,000	51
Pentanal	$CH_3[CH_2]_3CHO$	118	216	---	51
2-Methyl butane	$[CH_3]_2CH\ CH_2CH_3$	118	82	---	10
3-Methyl-2-butanone	$[CH_3]_2CH\ CO\ CH_3$	118	203		4
Cyclohexane	$\underbrace{CH_2[CH_2]_4CH_2}$	118	ca 178	13,000	1,4,7
2-Furyl methanol	$[C\ H\ O]CH_2OH$	117	ca 340	18,000	4
Tetrachloroethene	$Cl_2^4C^3= CCl_2$	116	250	---	2,3,6,7
2-Ethoxy-ethanol	$C_2H_5O[CH_2]_2OH$	116	275	17,000	4,5,7
1,3-Butanediol	$HO[CH_2]_2CH[OH]CH_3$	114	399	---	4
1,4-Butanediol	$HO[CH_2]_4OH$	114	455	20,000	4
Diethylamine	$[C_2H_5]_2NH$	112	133	18,000	51
1-Pentene	$CH_2 = CH[CH_2]_2CH_3$	111	ca 84	15,000	10
2-Methyl-tetrahydrofuran	$[C_4H_7O]\ CH_3$	110	ca 172		51
1-Methyl-1,4-epoxybutane	$CH_3\underbrace{CH[CH_2]_3O}$	110	149	20,000	4
Butanoic acid	$CH_3[CH_2]_2COOH$	108	327	20,000	51
Diethyl ether	$[C_2H_5]_2O$	106	94	18,000	1,6,7
1,1,1-Trichloroethane	$CH_3C\ Cl_3$	106	165	---	2,4
Ethyl acetate	$CH_3COOC_2H_5$	106	171	25,000	1,4,7,8

Table C-I (continued)

Pollutant	Chemical formula	V_m, cm³/mol	Boiling point, °F	LEL, ppm	Industry number
2-Methyl-2-propanol	$[CH_3]_3COH$	105	179	17,000	4
2-Methyl-1-propanol	$CH_3[CH_2]_2CH_2OH$	105		17,000	1,4
1-Butanol	$CH_3[CH_2]_3OH$	105	244	14,000	1,4,7
2-Butanol	$C_2H_5CH[OH]CH_3$	105	210	17,000	1,4
Phenol	C_6H_5OH	105	359	15,000	55,61
1,3-Pentadiene	$CH_3CH = CHCH = CH_2$	104	ca 109		4,6
Dimethyl disulfide	$[CH_3]_2S_2$	103	242		52
Tetrachloromethane	CCl_4	101	171	---	6,7
Cyclopentane	$CH_2[CH_2]_3CH_2$	100	120	---	1
Trichloroethene	$Cl_2C = C HCl$	98	188	---	2,3,6,7
1-Nitropropane	$C_3H_7NO_2$	97	266	26,000	1,4,7
2-Nitropropane	$[CH_3]_2CH NO_2$	97	248	26,000	1,4,7
Butane	$CH_3[CH_2]_2CH_3$	96	31	19,000	10
2-Methyl-propane	$[CH_3]_2CH CH_3$	96	14	18,000	10
Butanone	$C_2H_5COCH_3$	96	175	20,000	1,4,5,6,7,8, 51
2-Methyl-propanal	$[CH_3]_2CHCHO$	96	142	16,000	51
1,4-Dioxane	$O[CH_2]_2O CH_2CH_2$	96	214	20,000	7
Benzene	C_6H_6	95	176	14,000	1,4,6,7,51
Butanal	$CH_3[CH_2]_2CHO$	95	168	14,000	51
1,2-Propanediol	$HOCH_2CH[OH]CH_3$	92	ca 372	26,000	4
2-Methoxy-ethanol	$CH_3O[CH_2]_2OH$	92	253	23,000	1,4,7
Trimethylamine	$[CH_3]_3N$	92	38	20,000	51,52
1-Butene	$CH_2 = CHCH_2CH_3$	89	21	16,000	10
2-Methyl-propenal	$CH_2 = C[CH_3]CHO$	89	155	---	51
1,2-Dichloroethane	$Cl H_2CCH_2Cl$	88	182	62,000	6,7

Table C-I (continued)

Pollutant	Chemical formula	V_m, cm^3/mol	Boiling point, °F	LEL, ppm	Industry number
Tetrahydrofuran	$O[CH_2]_3CH_2$	88	147	20,000	7
Dimethyl sulfoxide	$[CH_3]_2SO$	86	372	26,000	4
Propanoic acid	CH_3CH_2COOH	86	286	29,000	51,61
2-Propanol	$[CH_3]_2CHOH$	84	180	23,000	1,4,7,9,51
1-Propanol	$CH_3CH_2CH_2OH$	84	206	21,000	1,4,7,51
Methyl acetate	CH_3COOCH_3	83	135	31,000	1,4,7
1,3-Butadiene	$CH_2 = CHCH = CH_2$	81	24	20,000	4,6
Butyne	$CH_3CH_2C \equiv CH$	81	46	---	6
Ethanethiol	CH_3CH_2SH	77	98	28,000	51,52
Ethanolamine	$H_2N\ CH_2CH_2OH$	75	338	---	7
Nitroethane	$CH_3CH_2NO_2$	75	239	34,000	1,4,7
Propanone	$[CH_3]_2CO$	74	133	30,000	1,4,5,7,51,61
Propane	$CH_3CH_2CH_3$	74	-48	22,000	10,57
Propanal	CH_3CH_2CHO	74	119	29,000	51,61
Propanenitrile	CH_3CH_2CN	73	206	31,000	6,51
Imidazol	$NH\ CH = NCH = CH$	72	492		51
Ethanediol	$HO[CH_2]_2OH$	70	388	32,000	4,51
Propene	$CH_2 = CH\ CH_3$	67	-54	20,000	57
Propenal	$CH_2 = CH\ CHO$	67	126	30,000	6,52,54
Propenenitrile	$CH_2 = CHCN$	66	172	30,000	6,51
Carbon disulfide	SCS	66	113	10,000	52

Table C-I (continued)

Pollutant	Chemical formula	V_m, cm^3/mol	Boiling point, °F	LEL, ppm	Industry number
Ethylamine	$C_2H_5NH_2$	66	63	35,000	51
Dichloromethane	CH_2Cl_2	65	104	155,000	2,5,7
Ethanoic acid	CH_3COOH	64	244	40,000	4,51,55,57,61, 63
Ethanol	CH_3CH_2OH	61	173	33,000	1,4,5,7,51,52,58
Propyne	$CH_3C \equiv CH$	59	-9	17,000	4
Methanethiol	CH_3SH	55	43	39,000	51,55
Ethanal	CH_3CHO	54	69	41,000	51
Nitromethane	CH_3NO_2	53	214	73,000	1,4,7,55
Ethanenitrile	CH_3CN	51	176		6
Sulfur dioxide	SO_2	42	14	---	6,63
Methanol	CH_3OH	42	149	60,000	1,4,7,55,57
Methanoic acid	$HCOOH$	42	212	180,000	57,61
Hydrogen sulfide	H_2S	33	-78	43,000	51,52
Methanal	$HCHO$	30	-6	40,000	57,60,61,63,65
Nitrogen dioxide	NO_2	27	70	---	63
Hydrogen chloride	HCl	25	---	---	65
Ammonia	NH_3	22	-27	160,000	51,57,60,63,65
Carbon monoxide	CO	22	---		63

Appendix C

Table C-II Flammability Characteristics of Organic Vapors in Air

Organic vapor	Molecular weight	Heat of combustion, Btu/ft^3	Auto-ignition temp. °F	LEL, ppm
Methane	16	1,050	997	50,000
Ethane	30	1,850	959	30,000
Propane	44	2,640	939	21,000
Butane	58	3,180	808	18,000
Pentane	72	4,200	543	14,000
Hexane	86	4,950	502	11,000
Heptane	100	5,760	477	12,000
Octane	114	6,530	464	10,000
Decane	142	6,870	446	8,000
Dodecane	170	9,080	417	6,000
Ethene	28	155	914	27,000
Propene	42	2,310	856	24,000
1-Butene	56	3,050	723	17,000
2-Butene	56	3,040	615	18,000
1,3-Butadiene	54	2,880	784	20,000
Ethyne	34	1,560	581	25,000
Benzene	78	3,920	1097	13,000
Toluene	92	4,520	1054	12,000
Ethyl benzene	106	5,480	860	10,000
Xylene	106	5,450	986	11,000
Cyclobutane	56	3,100	---	18,000
Cyclopentane	70	3,920	725	15,000
Cyclohexane	84	4,420	518	13,000
Cycloheptane	98	5,440	---	11,000
Methanol	32	797	702	67,000
Ethanol	46	1,640	792	33,000
1-Propanol	60	2,410	824	22,000
2-Propanol	60	2,380	752	20,000
1-Butanol	74	3,200	689	11,000
Dimethyl ether	46	1,730	662	34,000
Diethyl ether	74	3,030	356	19,000
Ethyl propyl ether	88	3,760	---	19,000
Ethanal	44	1,400	347	40,000
Propanal	58	2,010	---	37,000

Table C-II continued

Organic vapor	Molecular weight	Heat of combustion, Btu/ft^3	Auto-ignition temp. °F	LEL, ppm
Propanone	58	2,020	1000	26,000
2-Butanone	72	2,910	961	10,000
2-Pentanone	86	3,680	941	15,000
2-Hexanone	100	4,210	990	12,000
Ethyl acetate	88	2,690	939	22,000
Propyl acetate	102	-----	842	20,000
Isopropyl acetate	102	-----	860	18,000

Appendix D

Methods

Method for Calculating V_m

Additive Volume Increments to Calculate V_m, Method of LeBas

Element or factor	Increment, cm^3/mol
Carbon	14.8
Hydrogen	3.7
Oxygen	
Doubly bonded	7.4
Methyl ester and ethers	9.1
Ethyl ester and ethers	9.9
Higher esters and ethers	11.0
Acids	12.0
Joined to S, P, N	8.3
Nitrogen	
Primary amines	10.5
Secondary amines	12.0
Fluorine	8.7
Chlorine	21.6
Bromine	27.0
Iodine	----
Sulfur	25.6
Ring	
3-membered	- 6.0
4-membered	- 8.5
5-membered	-11.5
6-membered	-15.0
Naphthalene	-30.0
Anthracene	-47.5

To calculate V_m, the number of elements of each type in the molecule is multiplied by the volume increment for each corresponding element. The totals for each element are added to get the total molar volume. If the molecule contains ring structures, the corresponding volume increment is subtracted from the above total.

Lower Explosive Limits of Mixtures

Method for calculating lower explosive limit (LEL) of a mixture of combustible organic compounds, based on modified Le Chateliers' mixture law.

$$\text{LEL in \% conc.} = \frac{100}{P_1/N_1 + P_2/N_2 + P_3/N_3}$$

$P_1, P_2, P_3 \cdots P_n$ = volume % of each flammable vapor.

$N_1, N_2, N_3 \cdots N_n$ = volume % of each flammable vapor in air at the lower explosive limit.

For the mixture

		LEL of each vapor	
	P,%	N,%	ppm
2-Ethoxyethyl acetate	10.0	1.2	12,000
Toluene	36.3	1.4	14,000
Propanone	53.7	3.0	30,000

The calculated LEL for the mixture is 1.92% or 19,200 ppm.

Van der Waals' Constant a

Van der Waals' a is a force of attraction constant incorporated into the ideal gas equation to make it more generally applicable to nonideal vapors. The constant b is a volume factor related to the liquid volume of the vapor.

$pv = RT$	Ideal gas equation
$\left[p + \frac{a}{v^2}\right](v-b) = RT$	Van der Waals' equation of state

v is the molar gas volume at pressure p and temperature T.

CCl_4 Test Method

The apparatus used to determine CCl_4 capacity is shown in Figure D-1. The stepwise procedure employed is as follows:

1. Place approximately 1/2 gram of sample into a preweighed weighing bottle.
2. Heat samples to 110°C under vacuum, <1 mm Hg (valve 1 open, valve 2 closed).
3. After a few hours, remove vacuum, cap bottles and place in dessicator to cool.
4. Weigh bottles and replace in ovens with the caps again ajar.
5. Heat to 40°C under vacuum, <1 mm Hg.
6. Freeze CCl_4 in reservoir with cold bath of dry ice/acetone or methanol.
7. With vacuum still being applied, open valve 2 to evacuate the volume above the frozen CCl_4.
8. After 15 minutes, close valve 2 and remove cold bath, allowing CCl_4 to liquefy.
9. Apply wet ice bath around CCl_4 reservoir.
10. Close valve 1 and disconnect vacuum pump.
11. After CCl_4 temperature equals 0°C and oven temperature equals 40°C, open valve 2 SLOWLY.
12. After 3 hours, close valve 2 and open valve 1 to restore the oven to atmospheric pressure.
13. Recap bottles and place in dessicator to cool.
14. Reweigh bottles.
15. Compute % CCl_4 activity as follows:
    A. Sample weight = weight from 4 - weight of empty bottle

B. Weight CCl_4 picked up = weight from 14 - weight from 4

$$\% \ CCl_4 \text{ activity} = \frac{(B) - \text{blank}}{(A)} \times 100$$

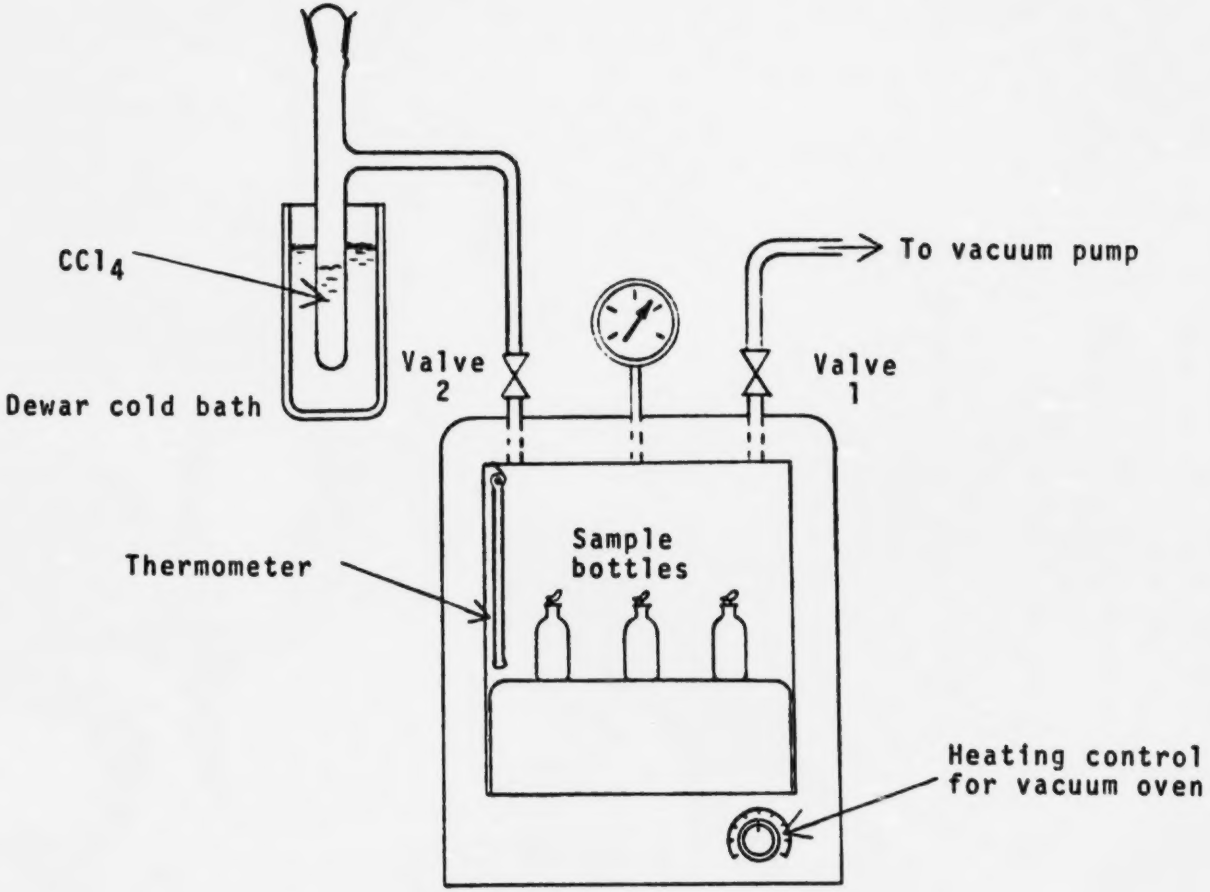


Figure D-1 Static CCl_4 Test Apparatus

Activated Carbon Regeneration

Two computer programs were written to simulate the desorption of organic compounds from activated carbon using heated air and steam as regenerating agents. These programs use heat and mass balances combined with the concept of theoretical adsorption stages to model the bed. Equation 19 of Chapter 4 is used to calculate the organic compound's vapor pressure over the carbon bed and this, in turn, used to calculate the latent heat of desorption. Equation 19, based on the Polanye potential theory of adsorption, is reproduced below with minor variations.

$$A = T/[2.3\ V_m]\ \ln\ [p_o/p] \qquad (1)$$

Correlation of Potential Equation with Amount Adsorbed

The data of the carbons and three organic compounds were fitted, using least square error techniques, to polynomial expressions as follows

$$\ln \omega = \alpha + \beta A + \gamma A^2 + \delta A^3 \qquad (2)$$

where ω is the amount adsorbed, measured in cm^3 liq/g.

The values of the constants α, β, γ and δ are given in Table D-I for the carbons.

The predicted value of A, given ω, is

$$A = \alpha + \beta \ln \omega + \gamma [\ln \omega]^2 + \delta [\ln \omega]^3 \qquad (3)$$

The values of the constants for Equation 3 are given in Table D-II.

In no case can A be less than zero. If a negative value is obtained, then ω has a larger value than the actual adsorptive capacity of the bed and unbound organic liquid exists. Under this circumstance the vapor pressure will equal that of the pure liquid and A is equal to zero.

Heat of Desorption

The latent heat of desorption is equal to the heat of vaporization of the pure organic liquid and its heat of wetting on the adsorbent. The heat of wetting can be related, using the Clausius-Clapeyron equation, to the vapor pressure

Table D-1 Numerical Values for the Constants of Equation 2

Carbon	A range	α	β	γ	δ
BPL V	0 <A<32	-0.781007	-9.119E-2	-5.90339E-3	7.63933E-5
BPL II	0 <A<12.5	-0.802935	-7.77809E-2	-4.94474E-3	---
	12.5<A	-0.182024	-0.189647	---	---
BPL VI	0 <A<10	-0.801228	-4.57639E-2	-5.00803E-3	---
	10 <A	-0.104591	-0.166206	---	---
GI	0 <A<17.5	-0.2421	-0.709226E-2	-8.13912E-3	---
	17.5<A<27.5	3.35328	-0.388684	-1.98237E-3	---

Table D-II Numerical Values for the Constants of Equation 3

Carbon	ω range	α	β	γ	δ
BPL V	ω<0.0125	1.67798	-4.19038	---	---
	ω>0.0125	-7.80764	-11.4475	-1.86287	-0.159537
BPL II	ω<0.078	-0.954685	-5.27179	---	---
	ω>0.078	-11.7179	-18.4925	-5.34297	-0.711735
BPL VI	ω<0.172	-0.628067	-6.01627	---	---
	ω>0.172	-26.0081	-50.3815	-26.7388	-5.53189
GI	ω<0.0175	9.06813	-2.09203	---	---
	ω>0.0175	-1.67587	-9.102	1.61275	-0.132675

of the adsorbed organic compound, which in turn can be predicted using the potential theory equation (Equation 1). The additional heat will be small for small A values, but will increase for the larger values.

The Clausius-Clapeyron equation has the form

$$\ln p_o = -\frac{\lambda}{RT} + k \tag{4}$$

where λ is the latent heat of vaporization of the pure liquid. When solved for ln p, the potential theory Equation 1 has the form

$$\ln p = \ln p_o - 2.3\ AV_m/T \tag{5}$$

By substitution of Equation 4 into 5, the following equation is derived which relates p to the heat of desorption ΔH.

$$\ln p = k - \frac{\lambda + 2.3\ AV_mR}{RT} \tag{6}$$

$$\Delta H = \lambda + 2.3\ AV_mR \tag{7}$$

Since A changes as the amount of organic compound is desorbed, the heat of desorption also varies. The amount of heat absorbed by the system can be found by integrating the heat of desorption over the amount desorbed. The equation for carrying out the integration has the form

$$Q = \frac{2.3\ V_mRW_c}{M} \int_{\omega_1}^{\omega_2} A\ d\omega, \tag{8}$$

where Q = Btu heat absorbed
R = gas constant, 3.42 Btu/[lb mol x °F]
W_c = lb carbon in bed
ω = lb organic/lb carbon
ω_1 ω_2 = lb organic/lb carbon at beginning and end of stage

The adsorption potential A is a function of ω. For concentrations such that A is large (small amount adsorbed) the plot of log ω versus A is a straight line. For small values of A, the plots can be considered straight lines on semi-log graphs if the amount of adsorbed organic compound does not vary over a factor of 2.

The integrated form of Equation 8 is as follows

$$\int_{\omega_1}^{\omega_2} A \, d\omega = [C_8-C_9][\omega_2-\omega_1] + C_9 \, [\omega_2 \ln\omega_2 - \omega_1 \ln\omega_1] \qquad (9)$$

Here

$$C_9 = \frac{A_2-A_1}{\ln\,[\omega_2/\omega_1]}$$

$$C_8 = A_1-C_9 \ln \omega_1$$

$A = A_2$ when $\omega = \omega_2$ and $A = A_1$ when $\omega = \omega_1$. The limit of $\omega_1 \ln \omega_1$ is zero when ω_1 approaches zero.

The derivation of the integral form of heat absorption equation, Equation 9, involved the following steps. Given a straight line potential plot, the following is true

$$A = C_8 + C_9 \ln \omega \qquad (10)$$

The integrals to be evaluated are

$$\int_{\omega_1}^{\omega_2} A \, d\omega = \int C_8 \, d\omega + \int C_9 \ln \omega \, d\omega \qquad (11)$$

Integrating the second expression by parts

$$\int_{\omega_1}^{\omega_2} A \, d\omega = C_8 \, \omega \Big]_{\omega_1}^{\omega_2} + C_9 \, \omega \ln \omega \Big]_{\omega_1}^{\omega_2} - C_9 \int_{\omega_1}^{\omega_2} d\omega$$

$$= [C_8-C_9][\omega_2-\omega_1] + C_9 \, [\omega_2 \ln\omega_2 - \omega_1 \ln\omega_1] \qquad (12)$$

The constants C_8 and C_9 are evaluated by solving simultaneously the following equations

$$A_2 = C_8 + C_9 \ln \omega_2$$

$$A_1 = C_8 + C_9 \ln \omega_1$$

This yields

$$C_9 = \frac{A_2 - A_1}{\ln [\omega_2/\omega_1]}$$

$$C_8 = A_1 - C_9 \ln \omega_1$$

Vapor Pressure of Pure Organic Liquid

The vapor pressure versus temperature relationships for water, trichloroethene, 4-methyl-2-pentanone and propanone were fitted by least mean square techniques to the equation

$$\ln p_0 = \alpha + \beta/T + C \ln T \qquad (13)$$

The numerical values for these constants are given in Table D-III.

Table D-III Numerical Values for Constants in Equation 12

Compound	Range °C	α	β	C
Water	25 to 100	50.1243	-6598.49	-4.35917
Trichloroethene	25 to 150	10.9567	-3686.53	1.00381
Propanone	25 to 150	39.3263	-4774.12	-3.14373
4-Methyl-2-pentanone	25 to 125	45.1415	-7059.07	-3.4225

Logic Diagram for Air-Regeneration

The programs make use of heat and mass balances and assume the organic vapors follow the perfect gas laws. There is little information available on heat and mass transfer coefficients, so a "theoretical plate" type of approach was used. The bed is divided into 32 theoretical segments and thermal and mass transfer equilibria are assumed at each segment. A given time increment is chosen, and the gas which enters during this interval is allowed to come to full equilibrium with the carbon. This gas then enters the next segment.

The logic diagram for air-regeneration is shown in Figure D-2. The heat and mass balances are carried out for each segment with a trial and error search for the amount

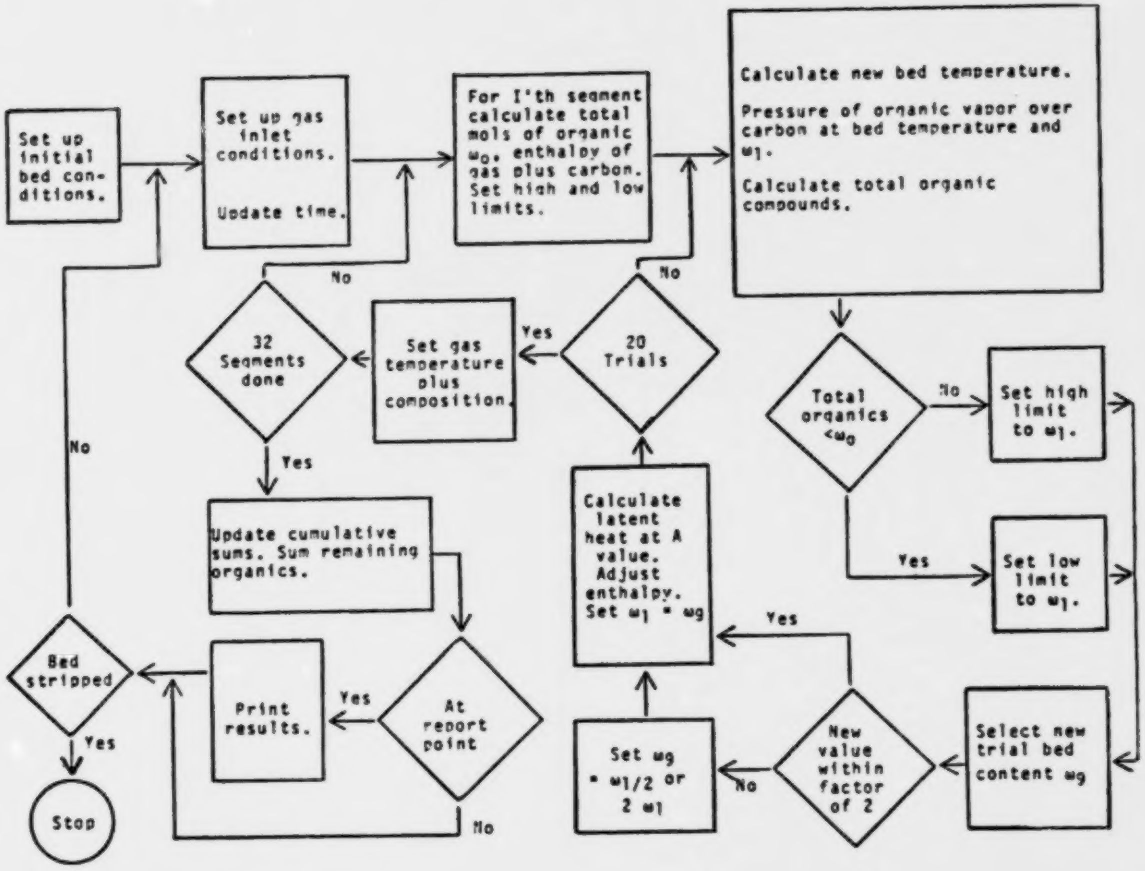

Set up initial bed conditions.
Set up gas inlet conditions.
Update time.
For I'th segment calculate total mols of organic ω_o, enthalpy of gas plus carbon. Set high and low limits.
Calculate new bed temperature.
Pressure of organic vapor over carbon at bed temperature and ω_1.
Calculate total organic compounds.
Total organics $<\omega_g$
No
Set high limit to ω_1.
Yes
Set low limit to ω_1.
Select new trial bed content ω_g
New value within factor of 2
Yes
No
Set ω_g = $\omega_1/2$ or 2 ω_1
Calculate latent heat at A value. Adjust enthalpy. Set ω_1 = ω_g
20 Trials
No
Yes
Set gas temperature plus composition.
32 Segments done
No
Yes
Update cumulative sums. Sum remaining organics.
At report point
Yes
No
Print results.
Bed stripped
No
Yes
Stop

Figure D-2 Logic Diagram for Air-Regeneration of organic compound remaining adsorbed on the bed. The heat of desorption is modeled exactly.

The following restrictions and assumptions are to be noted:

1. The heat capacity of the organic vapor and the air are constant with respect to temperature. For the temperatures occurring during stripping, this is satisfactory.
2. The bed contains 32 equilibrium stages. The program can be easily changed to give either fewer or greater stages. Going above 32 stages is not appreciably different; fewer stages will increase the amount of regenerant required.
3. The latent heat of the pure compound is constant with temperature.
4. The heat capacity of the organic compound on the carbon is equal to the gaseous heat capacity. This is a thermodynamic requirement once assumption No. 3 is made.
5. The organic vapor and the air follow the perfect gas laws.

Logic Diagram for Steam-Regeneration

Figures D-3 and -4 show the logic diagram for the steam system. The heat and mass balances are carried out for each segment, with a trial and error search for water content and the amount of adsorbed organic compound remaining on the bed. Again, the heat of desorption of the organic compound is modeled exactly.

This program permits several flow regimes to exist simultaneously:

1. The segment temperature is below an equilibrium temperature. The entering steam (if any) condenses on the bed and there is no exit steam.
2. The bed is at an equilibrium temperature. Steam condenses or water evaporates, depending on whether the sensible heat of the steam will supply the latent heat required by the organic compound.

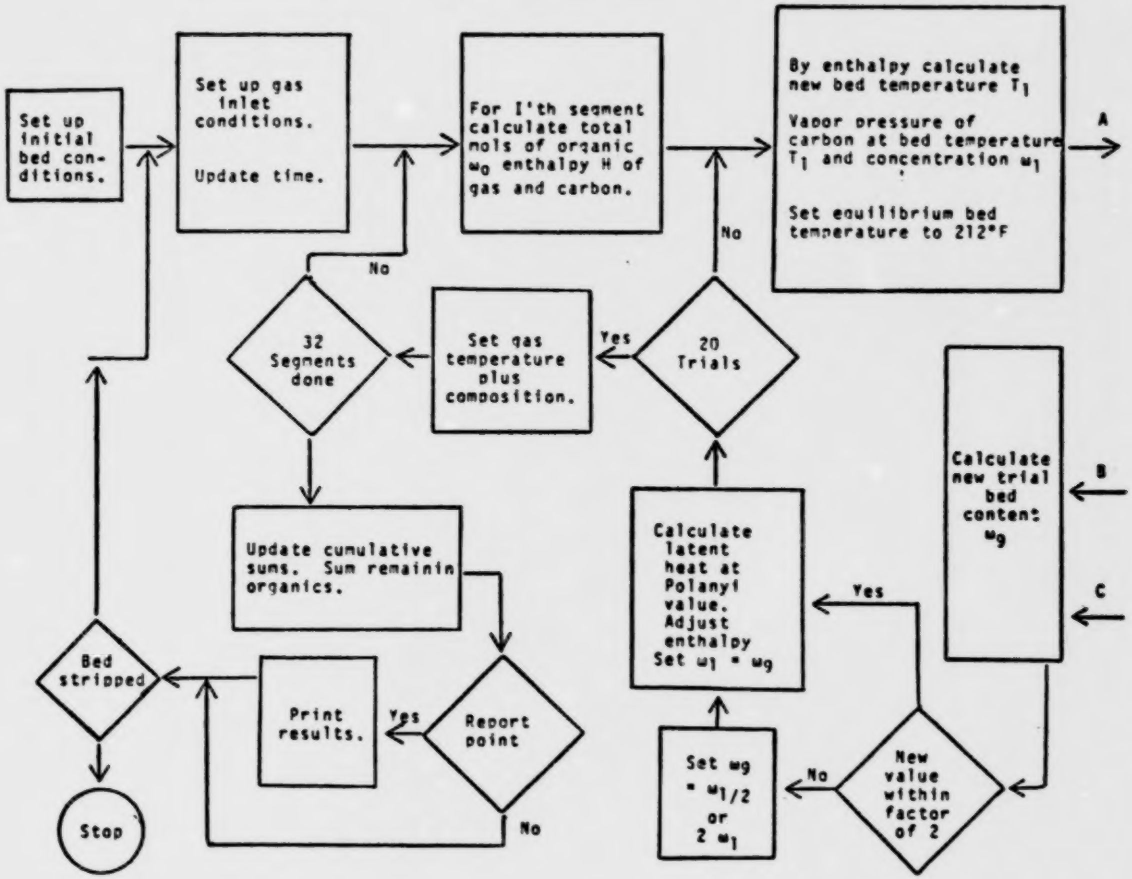

Set up initial bed conditions.
Set up gas inlet conditions. Update time.
For I'th segment calculate total mols of organic ω_0 enthalpy H of gas and carbon.
By enthalpy calculate new bed temperature T_1
Vapor pressure of carbon at bed temperature T_1 and concentration ω_1
Set equilibrium bed temperature to 212°F
A
No
20 Trials
Yes
Set gas temperature plus composition.
32 Segments done
No
Update cumulative sums. Sum remainin organics.
Report point
Yes
Print results.
No
Bed stripped
Stop
Calculate latent heat at Polanyi value. Adjust enthalpy Set $\omega_1 = \omega_g$
Yes
Calculate new trial bed content ω_g
B
C
New value within factor of 2
No
Set $\omega_g = \omega_1/2$ or $2\,\omega_1$

Figure D-3 Logic Diagram for Steam-Regeneration

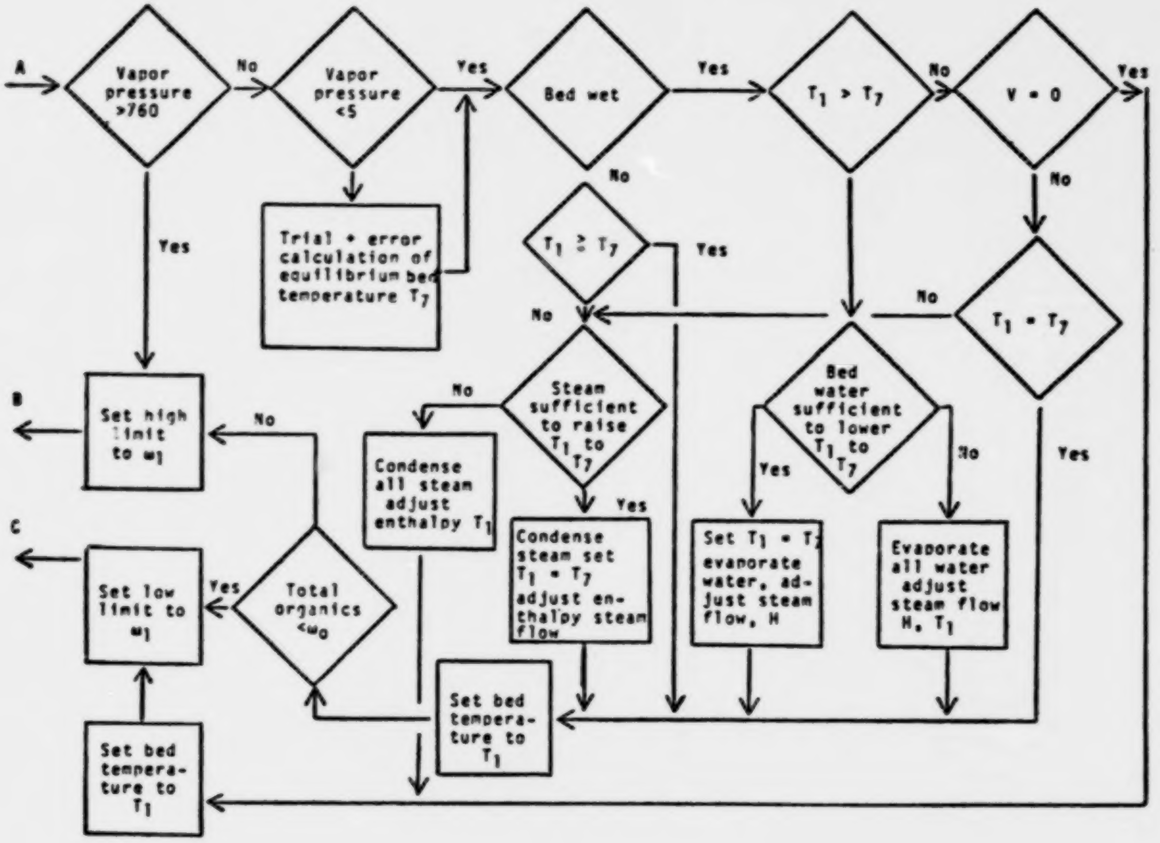

A
Vapor pressure >760
No
Yes
Vapor pressure <5
Trial + error calculation of equilibrium bed temperature T_7
Yes
Bed wet
Yes
No
$T_1 > T_7$
No
V = 0
Yes
No
$T_1 \geq T_7$
Yes
No
$T_1 = T_7$
No
Yes
Steam sufficient to raise T_1 to T_7
No
Yes
Bed water sufficient to lower T_1 to T_7
Yes
No
Set high limit to w_1
B
Condense all steam adjust enthalpy T_1
Condense steam set $T_1 = T_7$ adjust enthalpy steam flow
Set $T_1 = T_7$ evaporate water, adjust steam flow, H
Evaporate all water adjust steam flow H, T_1
No
Total organics $<w_0$
Yes
Set low limit to w_1
C
Set bed temperature to T_1
Set bed temperature to T_1

Figure D-4 Logic Diagram for Steam-Regeneration, Figure D-3 continued

3. The bed is dry and above the equilibrium temperature. For this case, stripping proceeds like the gas stripping case.

The equilibrium temperature is the temperature at which the organic vapor pressure and the steam total one atmosphere.

The previously noted restrictions and assumptions still apply with the following additions:

1. The program is written specifically for steam as regenerating agent. Other fluids would require minor program changes.
2. There is assumed to be no interaction between the organic compound and the steam. In particular, there is no displacement effect where the steam will "salt out" the organic. If displacement occurs, the effect would be to lower the steam requirement.
3. The latent heat of adsorbing water on carbon is small. The program ignores the latent heat of wetting and considers the water vapor pressure to be equal to that of pure fluid.
4. The latent heat of evaporation of water is constant with temperature. This requires the heat capacity of steam and water to be the same. Although steam has a heat capacity about half of that of water, this effect should be small because the majority of the heat is provided by the latent heat.

Appendix E
Sample Calculations

Heat of Adsorption
(from page 4-31)

The following demonstrates the procedure for calculating the heat of adsorption using the Clausius Clayeyron equation

$$\ln p = \frac{\Delta H}{RT} + k \tag{1}$$

The data for making the calculations were selected from Table 4-IX for $\omega = 0.30$ cm^{3}liq/g . When the pressure data for the three temperatures -9°F (250°K), 77°F (298°K) and 170°F (350°K) are substituted into Equation 1, the three following equations are obtained which can now be solved simultaneously in pairs:

$$\text{at } -9°\text{F},\ \ln 2.3 = \frac{\Delta H}{2 \times 250} + k \tag{2}$$

$$\text{at } 77°\text{F},\ \ln 38 = \frac{\Delta H}{2 \times 298} + k \tag{3}$$

$$\text{at } 170°\text{F},\ \ln 340 = \frac{\Delta H}{2 \times 350} + k \tag{4}$$

$$0.833 = 2.000 \times 10^{-3}\ \Delta H + k \tag{2}$$

$$3.638 = 1.678 \times 10^{-3}\ \Delta H + k \tag{3}$$

$$5.830 = 1.428 \times 10^{-3}\ \Delta H + k \tag{4}$$

By subtracting Equation 2 from 3

$$2.805 = -0.322 \times 10^{-3}\ \Delta H;\ \Delta H = -\underline{8{,}710}\ \text{cal/mol}$$
$$k = 18.2$$

By subtracting Equation 3 from 4

$$2.192 = -0.250 \times 10^{-3}\ \Delta H;\ \Delta H = -\underline{8{,}760}\ \text{cal/mol}$$
$$k = 18.3$$

If a generalized adsorption curve is available for the carbon being considered, an estimate of ΔH can be made with knowledge of only the physical properties of the organic vapor. See Potential Theory Equations, Chapter 4, for discussion.

To demonstrate the procedure generalized adsorption curve of Figure 4-10 (or BPL II curve of Figure 4-12) was selected and the calculations carried out for butane at $\omega = 0.25$ cm³liq/g.

From the curve at $\omega = 0.25$ cm³liq/g, A = 6.75; or

$$6.75 = [T/V_m] \log [p_0/p] \qquad (5)$$

By substituting two values of T and the corresponding p_0 into Equation 5, two p values can now be calculated. The two T and p values are sufficient data to calculate ΔH with Equation 1.

For the calculations T = 298°K and 350°K were selected. The corresponding p_0 are 1820 and 7000 mm of Hg. $V_m = 96.2$ cm³/mol. The pair of equations are as follows

$$\text{at } 298°K,\ 6.75 = [298/96.2] \log [1820/p] \qquad (6)$$

$$\text{at } 350°K,\ 6.75 = [350/96.2] \log [7000/p] \qquad (7)$$

at 298°K p = 11.7 mm of Hg

at 350°K p = 97.7 mm of Hg

The above substituted into Equation 1 give

$$\ln 11.7 = \frac{\Delta H}{2\text{x}298} + k \qquad (8)$$

$$\ln 97.7 = \frac{\Delta H}{2\text{x}350} + k \qquad (9)$$

The above pair of equations solved simultaneously gives

$\Delta H = -8{,}500$ cal/mol

$k = 16.9$ (ave)

Free Energy of Adsorption

Calculation of ΔF for $\omega = 0.10$ cm³liq/g in Table 4-12 using p_o and f_o in equations below at 100°, 150°, 200° and 250°F.

$$\Delta F = -RT \ln [p_o/p] \qquad (1)$$

$$\Delta F = -RT \ln [f_o/p] \qquad (2)$$

Here $R = 1.98 \cong 2.0$ cal/(°C x mol)

To calculate ΔF for $\omega = 0.1$ cm³liq/g in Table 4-12 the following values for T, p_o and p, Table E-I below were used in Equation 1 above.

Table E-I Data Used for Calculating ΔF in Table 4-12

Temperature			p	
°F	T	p_o, atm	mm of Hg	atm
100	311	13.0	23.5	0.0309
150	339	23.0	50	0.0658
200	366	38.0	87	0.114
250	394	60.0	155	0.204

To recalculate ΔF using fugacity instead of pressure, only f_o need be considered since at the low vapor pressures under consideration $f = p$. The fugacity f_o for propane liquid can be obtained approximately by using van der Waals' Equation of State, Equation 3 below, and Equation 4 based on Equation 3.

$$p_o + \frac{a}{V^2} [V-b] = RT \qquad (3)$$

$$\ln f_o = \ln \frac{RT}{V-b} + \frac{b}{V-b} - \frac{2a}{RTV} \qquad (4)$$

In Equation 4, a is a function of the forces of attraction between molecules and b is the ultimate van der Waals' volume of the vapor in its compressed state. When p_o is measured in atmospheres and V in liters, a for propane is 8.66 liter² x atm/mol² and b is 0.0844 liters/mol. These constants are obtainable for many vapors from organic and physical chemistry handbooks. Here R = 0.082 liters/(°C x mol).

With appropriate substitutions of p_o and T from Table E-I into Equation 3, the following numerical values were calculated for V.

T	V, l/mol
311	1.60
339	0.910
366	0.450
394	0.198

By substituting the above V and other appropriate values for T, a and b into Equation 4, the following numerical values were calculated for f_o.

T	f_o, atm
311	12.0
339	18.8
366	26.8
394	39.4

With above numerical value of f_o and other appropriate values for T and p substituted into Equation 2, the ΔF as given in Table E-II were calculated.

Table E-II ΔF Based on p_o and f_o

	ΔF, cal/mol	
T	p_o	f_o
311	3,760	3,710
339	3,970	3,830
366	4,250	3,960
394	4,480	4,140

Adsorption Zone
(from page 4-48)

The adsorption zone length, L_z, and the mean adsorptive capacity ω_z of the adsorption zone are calculated for the vapor distribution curve given in Figure 4-15 according to the following procedure from data derived from the effluent concentration curve given in Figure 4-14 and additional data given below. The adsorption data below and the curve in Figure 4-14 were obtained from Lockheed (1966) Run Number 119 for Barnebey Cheney AC carbon. This carbon is similar to SXA at A = 17.2 and larger.

Adsorbent - Barnebey Cheney AC
Mesh size - 28 to 60
Vapor - Butane
T - 43.8°C; 317°K
P - 5 $\mathrm{lb/in^2}$ absolute

F - 0.223 l/min at P = 5 $\mathrm{lb/in^2}$ abs.
C_i - 66.8 ppm at P = 5 $\mathrm{lb/in^2}$ abs.
W - 0.488 g
D - 0.8 cm
A_c - 0.502 $\mathrm{cm^2}$

L - 2.4 cm
ω - $2.98 \times 10^{-2}\,\mathrm{cm^3 liq/g}$
A - 17.2

By a summing-up process the amount of butane penetration can be calculated from the effluent concentration curve in Figure 4-14. When the summation is carried from C = 0.01 C_i to C = C_i, the penetrated amount is equivalent to the amount adsorbed in the adsorption zone. The summation as given below was in Δt increments of 50 min.

Δt	Mean C ($\bar{C}$), ppm
600-650	1
650-700	3
700-750	11
750-800	27
800-850	49
850-900	59
900-950	63
950-975	65/2
	245

$$\Sigma \Delta t \bar{C} = 50 \times 245 = 12{,}200$$

To convert $\Sigma\Delta tC$ to butane weight penetrated, it is multiplied by

$$\frac{P}{14.7} \times \frac{273}{T} \times \frac{F}{22.4} \times M \times 10^{-6} = 1.69 \times 10^{-7}$$

$$\Sigma\Delta t\bar{C} \times 1.69 \times 10^{-7} = 0.00206 \text{ g}$$

Weight of butane entering carbon bed between t = 600 and 975 min is,

$$[975-600] \times C_i \times 1.69 \times 10^{-7} = 0.00418 \text{ g}$$

Residual capacity or amount adsorbed in time interval t = 600 to 975 min is,

$$0.00418-0.00206 = 0.00212 \text{ g}$$

The total amount of butane the 0.488 g of carbon can adsorb is the amount adsorbed in time t = 0 to 600.

$$\begin{aligned} 600 \times C_i \times 1.69 \times 10^{-7} &= 0.00677 \\ \text{plus residual capacity} &= \underline{0.00212} \\ \text{total amount} &= 0.00889 \text{ g} \end{aligned}$$

The adsorptive capacity of the carbon is,

$$0.00889/W = 0.0182 \text{ g/g; } 0.0302 \text{ cm}^3 \text{ liq/g}$$

The amount adsorbed in the saturated bed length L_s is equal to the capacity of the total bed minus the residual capacity and amount adsorbed in the adsorption zone, i.e.,

$$0.00889 - [0.00206 + 0.00212] = 0.00471 \text{ g}$$

The saturated bed length is then

$$L_s = \frac{0.00471}{0.0182} \times \frac{L}{W} = 1.27 \text{ cm}$$

The adsorption zone length is

$$L_z = 2.40-1.27 = 1.13 \text{ cm}$$

The adsorptive capacity of the saturated bed is

$$\omega_s = \frac{0.00889}{LA_c} = 0.00738 \text{ g/cm}^3$$

The mean adsorptive capacity of the adsorption zone is

$$\omega_z = \frac{0.00206}{L_z A_c} = 0.00363 \text{ g/cm}^3$$

To check the self consistancy of the above numerical values, they may be substituted into Equation 4-23. If correct, t_b should be equal to 600 min. C_i substituted into Equation 4-23 is first converted from ppm at reduced pressure to g/l, as follows:

$$C_i = 66.8 \text{ ppm } \frac{P \; 273 \; M \; 10^{-6}}{14.7 \; T \; 22.4} = 5.06 \times 10^{-5} \text{ g/l}$$

$$t_b = \frac{A_c}{FC_i}[\omega_s L_s + \omega_z L_z] \qquad (23)$$

$$t_b = \frac{0.502}{0.223 \times 5.06 \times 10^{-5}} \times [0.00738 \times 1.27 + 0.00363 \times 1.13]$$

$$t_b = 600 \text{ min}$$

Calculation of L_c at Different C_b/C_i (from page 4-52)

Using Equation 27 of Chapter 4, given below, L_c values were calculated at different C_b/C_i using ω_s, ω_z, L_z and the effluent concentration curve in Figure 4-14.

$$L_c = \left[\frac{\omega_s - \omega_z}{\omega_s}\right] L_z - \frac{C_i F f [t_b - t_1]}{\omega_s A_c} \qquad (27)$$

Here
$C_i = 66.5$ ppm
$F = 0.223$ l/min at 5 lb/in² pressure
$A_c = 0.502\ \text{cm}^2$
$\omega_s = 0.00738\ \text{g/cm}^3$ of carbon
$\omega_z = 0.00363\ \text{g/cm}^3$ of carbon
$L_z = 1.13$ cm

$$\text{Factor } f = \frac{P\ 273\ M\ 10^{-6}}{14.7\ T\ 22.4} = 7.6 \times 10^{-7}$$

where $P = 5\ \text{lb/in}^2$, $T = 317°\text{K}$ and $M = 58$ g/mol. The time interval $[t_b - t_1]$ is measured on the effluent concentration curve from $C = 0.01\ C_i$ to $C = C_i$. It is related to C_b/C_i as given in the following table.

$[t_b - t_1]$	C_b/C_i
625-600	0.02
675-600	0.06
725-600	0.17
775-600	0.41
790-600	0.50
825-600	0.75
875-600	0.89
925-600	0.94
975-600	0.96
1025-600	0.98
1075-600	1.00

The quantity

$$\left[\frac{\omega_s - \omega_z}{\omega_s}\right] L_z = 0.57\ \text{cm}$$

The following is a summary of the calculations according to Equation 4-27.

C_b/C_i	$[t_b-t_1]$	$\dfrac{C_iFf[t_b-t_1]}{\omega_sA_c}$, cm	L_c, cm
0.01	0	0.0	0.57
0.02	25	-0.08	0.49
0.06	75	-0.23	0.34
0.17	125	-0.38	0.19
0.41	175	-0.53	0.04
0.50	190	-0.58	-0.01
0.75	225	-0.69	-0.12
0.89	275	-0.84	-0.27
0.94	325	-0.99	-0.42
0.96	375	-1.14	-0.57
0.98	425	-1.30	-0.73
1.00	475	-1.45	-0.88

To calculate service time, t, when L_c is known at any C_b,

$$t = \frac{\omega_sA_c}{C_iFf}\,[L-L_c],$$

$$t\ [\text{when } C_b = 0.01\ C_i] = \frac{0.00738 \times 0.502}{66.5 \times 0.223 \times 7.6 \times 10^{-7}}\,[2.40-0.57]$$

$= 600$ min,

$$t\ [\text{when } C_b = C_i] = 327\ [2.40 + 0.88] = 1070 \text{ min.}$$

Calculation of L_z and L_c, Klotz Equation
(from page 4-57)

The following is a sample calculation for 4-methyl-2-pentanone, using Klotz Equation 4-28.

$$L_z = \frac{2.3}{a}\left[\frac{D_p U_m \rho}{\mu}\right]^{0.41}\left[\frac{\mu}{\rho D_v}\right]^{0.67}\log\,[C_i/C_b]$$

$$+\ 2.30\ k\ U_m \log\,[C_i/C_b]$$

The following conditions are fixed:

D_p = 0.35 cm; 4 to 10 mesh
U^p = 100 ft/min; U_m is measured in cm/sec
ρ for air = 1.20×10^{-3} g/cm^3 at 77°F
μ for air = 1.83×10^{-4} g/(cm x sec) at 77°F
C_i/C_b = 100

$\log C_i/C_b$ = 2
T = 77°F; 298°K
k = 0.0035
$a = \dfrac{[1-\varepsilon]6}{D_p}$

ε, the void volume between carbon particles, varies between 0.3 to 0.4. When $\varepsilon = 0.4$, $a \sim 3.6/D_p$.

$U = U_m\,[60/30.5]\,\varepsilon^{2/3} = 1.066\ U_m$

$U_m^{0.41} = 0.97\ U^{0.41}$

In Equation 4-28

$$\frac{2.3}{a} = \frac{2.3}{3.6} D_p = 0.638\ D_p$$

$$\left[\frac{U_m \rho}{\mu}\right]^{0.41} = \frac{0.97\ U^{0.41} \times [1.20 \times 10^{-3}]^{0.41}}{[1.83 \times 10^{-4}]^{0.41}} = 2.095\ U^{0.41}$$

$$\left[\frac{\mu}{\rho}\right]^{0.67} = 0.284$$

$$\log\,[C_i/C_b] = 2$$

$$L_z = 0.638 \times 2.095 \times 0.284 \times 2\ D_p\ D_p^{\,0.41} U_m^{0.41}\ D_v^{-0.67}$$

$$+\ 0.008\ U_m \times 2$$

$$L_z = 0.80\ D_p^{1.41} U_m^{0.41}\ (1/D_v)^{0.67} + 0.016\ U_m$$

When the numerical values are substituted for D_p, U_m and D_v, ($D_v = 0.070\ \text{cm}^2/\text{sec}$)

$$L_z = 7.2 + 1.6 = \underline{\underline{8.8\ \text{cm}}};\ \underline{\underline{3.5\ \text{in.}}}$$

$$L_c = 8.8 \times 0.77 = \underline{\underline{6.9\ \text{cm}}};\ \underline{\underline{2.7\ \text{in.}}}$$

Calculations for Adsorbed-Vapor Profile as Presented in Figure 4-18

Conditions for Adsorption of Ternary Solvent Mixture

	C_i
Total concentration	- 500 ppm
2-Ethoxyethyl acetate	- 50 " ; 1.68×10^{-5} lb/ft^3
Toluene	- 181 " ; 4.25×10^{-5}
Propanone	- 268 " ; 3.96×10^{-5}

Solvent properties

	Symbol	M	V(1)	V_m	C_o ppm
2-Ethoxyethyl acetate	E	132	135	163	3,400
Toluene	T	92	106	118	37,000
Propanone	P	58	73	74	290,000

Total vapor-air flow, F - 3,000 ft^3/min
Vapor-air velocity, U - 110 ft/min

Carbon bed area, A_c - 3,930 in^2
Carbon particle size, D_p - 4 to 10 mesh; 0.35 cm
Carbon density - 0.50 g/cm^3; 0.018 lb/in^3

Service time, t_b - 8 hr
Break concentration, C_b - 0.01 C_i
Vapor-air temperature, T - 25°C; 298°K

(1) Molar volume at 25°C

Adsorptive capacity at influent concentration

$$A = T/V_m \log [C_o/C_i]$$

E $\quad A = 1.83 \log [3400/50] = 3.36$

T $\quad A = 2.52 \log [37{,}000/181] = 5.81$

P $\quad A = 4.03 \log [290{,}000/268] = 12.1$

From the BPL generalized adsorption curve in Figure 4-12 the ω_s values given below were determined.

E $\quad \omega_s = 0.31$ cm^{3}liq/g
T $\quad \omega_s = 0.23$ cm^{3}liq/g
P $\quad \omega_s = 0.074$ cm^{3}liq/g

To convert above ω_s in cm³liq/g to lb/in bed length, the equation given below was used.

$$0.018\ [M/V_m]\ A_c\ [\omega_s\ \text{cm}^3\text{liq/g}] = \omega_s\ \text{lb/in}$$

E $\omega_s = 17.8$ lb/in Zone 1
T $\omega_s = 12.7$ lb/in Zone 3
P $\omega_s = 4.10$ lb/in Zone 5

Length of adsorption zone, L_z

From Figure 4-17, L_z was determined at $U = 110$ ft/min for each vapor at the corresponding V.

E $L_z = 3.6$ in Zone 2
T $L_z = 3.3$ in Zone 4
P $L_z = 2.9$ in Zone 6

From Equation 4-26 and also Page 4-54,

$$\left[\frac{\omega_s - \omega_z}{\omega_s}\right] = 0.77$$

E $\omega_z = 4.1$ lb/in average, when $\omega_s = 17.8$ lb/in
T $\omega_z = 2.9$ " " " $\omega_s = 12.7$ lb/in
P $\omega_z = 0.95$ " " " $\omega_s = 4.1$ lb/in

Total amount adsorbed in L_z

E $3.6 \times 4.1 = 14.8$ lb Zone 2
T $3.3 \times 2.9 = 9.6$ lb Zone 4
P $2.9 \times 0.95 = 2.8$ lb Zone 6

Total amount adsorbed

$$Ft_bC_i = 3{,}000 \times 8 \times 60\ C_i = 1.44 \times 10^6\ C_i$$

E $1.44 \times 10^6 \times 1.68 \times 10^{-5} = 24.2$ lb
T $1.44 \times 10^6 \times 4.25 \times 10^{-5} = 61.2$ lb
P $1.44 \times 10^6 \times 3.96 \times 10^{-5} = 57.0$ lb

Total 142.4 lb

Amount adsorbed in Zones 1, 3 and 5

E $24.2 - 14.8 = 9.4$ lb

T $61.2 - 9.6 = 51.6$ lb

P $57.0 - 2.8 = 54.2$ lb

Length of Zones 1, 3 and 5

E $9.4/17.8 = 0.5$ in Zone 1

T $51.6/12.7 = 4.1$ in Zone 3

P $54.2/4.1 = 13.2$ in Zone 5

Shape of adsorption zone profile is assumed to be identical to the vapor-phase curve as calculated from log $[C_i/C]$ in Equation 4-29. In these calculations

$$L = k_2 \log\,[\omega_s/\omega]\Big]_{\omega\,=\,0.01\,\omega_s}^{\omega\,=\,\omega_s}$$

$L = 0$ when $\omega_s/\omega = 1.0$ and

$L = L_z$ when $\omega_s/\omega = 100$.

Calculations for Adsorbed-Vapor Profile as Presented in Figure 4-19

Conditions are the same as for adsorbed-vapor profile presented in Figure 4-18 except coadsorption is taken into consideration.

Equations for calculating coadsorption

E $C_1 = X_1 C_{01} [\omega_t]$

T $C_2 = X_2 C_{02} [\omega_t]$

P $C_3 = X_3 C_{03} [\omega_t]$

C_1, C_2 and C_3 are the equilibrium adsorption vapor pressures of E, T and P, respectively. X_1, X_2 and X_3 are the mole fractions of adsorbed E, T and P. C_{01} is the calculated equilibrium vapor pressure of E when the weight of adsorbed E is assumed equal to the sum of the actual adsorbed weights of E, T and P. This is also true for C_{02} and C_{03}. In these calculations C_1, C_2 and C_3 are always known for the saturated carbon zones. C_{01}, C_{02} and C_{03} were estimated from the generalized adsorption curve for BPL carbon in Figure 4-12. By trial-and-error, C_{01}, C_{02} and C_{03} are calculated at different $[\omega_t]$ until $X_1 + X_2 + X_3 = 1.0$. To simplify calculations, $[\omega_t]$ cm^{3}liq/g was not corrected for differences in liquid densities of E, T and P. For Zone 1 of Figure 4-19, the $[\omega_t]$ that gives $X_1 + X_2 + X_3 = 1.0$ is 0.32 cm^{3}liq/g at $A = 3.28$.

The following sets of calculations give the steps in determining X_1, X_2 and X_3 and the amount of E, T and P adsorbed per inch of bed length.

Adsorption potential equations

$$A = [T/V_m] \log [C_o/C_i]$$

E $A = 1.83 \log [3{,}400/C_{01}]$

T $A = 2.52 \log [37{,}000/C_{02}]$

P $A = 4.03 \log [290{,}000/C_{03}]$

C_{01}, C_{02} and C_{03} for Zone 1

At A = 3.28, found by trial-and-error:

E $3.28/1.83 = \log [3{,}400/C_{01}] = 1.79$

T $3.28/2.52 = \log [37{,}000/C_{02}] = 1.30$

P $3.28/4.03 = \log [290{,}000/C_{03}] = 0.814$

$C_{01} = 55$ ppm

$C_{02} = 1{,}860$ ppm

$C_{03} = 44{,}500$ ppm

X_1, X_2 and X_3 for Zone 1

$X_1 = 50/55 = 0.910$

$X_2 = 181/1{,}860 = 0.097$

$X_3 = 268/44{,}500 = \underline{0.006}$

1.013

Pounds of E, T and P adsorbed per inch of bed length in Zone 1

Mol fractions converted to liquid volume fractions, $[XV_m]$.

		Liq vol fraction
E	0.910 x 163 = 148	0.925
T	0.097 x 118 = 11.4	0.071
P	0.006 x 74 = 0.44	0.0027
	160	0.999

Liquid volume fraction converted to lb/in.

$\omega_s = 0.018$ [liq vol fraction] $[\omega_t]$ $[M/V_m]$ A_c = lb/in

E	0.018 ×	0.925 ×	0.32 ×	0.81 ×	3,930	=	16.9 lb/in
T		0.071		0.78		=	1.2 lb/in
P		0.0027		0.78		=	0.05 lb/in
					Total		18.1

Pounds of T and P adsorbed per inch of bed length in Zone 3 at influent concentrations, first approximation

T $C_2 = X_2 C_{02} [\omega_t] = 181$ ppm

P $C_3 = X_3 C_{03} [\omega_t] = 268$ ppm

By trial-and-error, $X_2 + X_3 = 1.0$ when $[\omega_t] = 0.227$ cm³ liq/g at A = 5.8.

T	$X_1 =$	0.977
P	$X_2 =$	0.025
		1.002

Mol fraction converted to liquid volume fraction and lb/in bed length.

		Liq vol fraction
T	0.977 x 118 = 115	0.983
P	0.025 x 74 = 1.85	0.0158
	117	0.999

T $\omega_s = 0.018 \times 0.983 \times 0.227 \times 0.78 \times 3{,}930 =$ 12.3 lb/in

P $\omega_s =$ 0.0158 0.78 = 0.20 lb/in

Rate of desorption of T and P in Zone 2, second approximation

The 12.3 lb/in of T and 0.20 lb/in of P are partially desorbed by the adsorption front of E moving at the rate of

$FC_1/[\omega_s$ for E], in/min.

$3{,}000 \times 1.68 \times 10^{-5}/16.9 = 2.98 \times 10^{-3}$ in/min

T $12.3 - 1.2 = 11.1$ lb/in desorbed
P $0.20 - 0.05 = 0.15$ lb/in desorbed

T $11.1 \times 2.98 \times 10^{-3} = 3.31 \times 10^{-2}$ lb/min
P $0.15 \times 2.98 \times 10^{-3} = 0.45 \times 10^{-3}$ lb/min

Concentration of desorbed vapors

T $3.31 \times 10^{-2}/3{,}000 = 1.10 \times 10^{-5}$ lb/ft³
P $0.45 \times 10^{-3}/3{,}000 = 0.15 \times 10^{-6}$ lb/ft³

T $[1.10 \times 10^{-5} \times 392/92]\ 10^{6} = \underline{47}$ ppm
P $[0.15 \times 10^{-6} \times 392/58]\ 10^{6} = \underline{1}$ ppm

Concentration of vapors in Zone 3, second approximation

T $181 + 47 = 228$ ppm
P $268 + 1 = 269$ ppm

Pounds T and P adsorbed in Zone 3, second approximation

T $C_2 = X_2 C_{02}\ [\omega_t] = 228$ ppm
P $C_3 = X_3 C_{03}\ [\omega_t] = 269$ ppm

By trial-and-error, $X_2 + X_3 = 1.0$ when $[\omega_t] = 0.235$ cm³ liq/g at $A = 5.55$.

		Liq vol fraction
T	$X_1 = 0.975$	0.987
P	$X_2 = 0.022$	0.0138
	0.997	1.008

T $\omega_s = 0.018 \times 0.987 \times 0.235 \times 0.78 \times 3{,}930 = 12.8$ lb/in
P $\omega_s =$ 0.0138 0.78 $= 0.18$ lb/in

Rate of desorption of T and P in Zone 2, third approximation

T 2.98×10^{-3} in/min $[12.8 - 1.2] = 3.46 \times 10^{-2}$ lb/min

P 2.98×10^{-3} in/min $[0.18 - 0.05] = 0.39 \times 10^{-2}$ lb/min

Concentration of desorbed vapors

T $3.46 \times 10^{-2}/3{,}000 = 1.15 \times 10^{-5}$ lb/ft^3; 49 ppm
P $0.39 \times 10^{-2}/3{,}000 = 0.13 \times 10^{-6}$ lb/ft^3; 1 ppm

Concentration of vapors in Zone 3, third approximation

T $181 + 49 = 230$ ppm
P $268 + 1 = 269$ ppm

The third approximation made very little change in vapor concentration; the values for ω_s on the second approximation will be used.

Pounds of P adsorbed per inch of bed length in Zone 5 at influent concentration, first approximation

At $C_3 = 268$ ppm, $A = 12.2$

$A = 4.03 \log [290{,}000/268] = 12.2$

$\omega_s = 0.072$ cm^{3}liq/g; 4.02 lb/in

Rate of desorption of P in Zone 4, second approximation

The 4.02 lb/in of P is partially desorbed in Zone 4 by the adsorption front of T moving at the rate of

$FC_2/[\omega_s$ for T], in/min,

$3{,}000 \times 5.40 \times 10^{-5}/12.8 = 1.27 \times 10^{-2}$ in/min.

P $1.27 \times 10^{-2} [4.02 - 0.18] = 4.86 \times 10^{-2}$ lb/min

Concentration of P in Zone 5, second approximation

Desorbed P $4.86 \times 10^{-2}/3{,}000 = 1.62 \times 10^{-5}$ lb/ft^3; 109 ppm
Total P concentration $= 268 + 109 = 377$ ppm

Pounds of P adsorbed per inch of bed length in Zone 5, second approximation

At $C_3 = 377$, $A = 11.6$, $\omega_s = 0.083$ or 4.60 lb/in

Pounds of P adsorbed in Zone 6

From Figure 4-17, L_z is 2.9 in. at U = 110 ft/min and V = 73 cm³/mol. From Equation 4-26 and also Page 4-54,

$$\left[\frac{\omega_s-\omega_z}{\omega_s}\right] = 0.77$$

ω_s is 4.60 lb/in and by the above equation, ω_z is 1.06 lb/in average capacity. Total amount P adsorbed in Zone 6 is

$$2.9 \times 1.06 = \underline{3.10 \text{ lb}}$$

In Zone 2, E is being adsorbed while T and P are desorbed. The changes taking place are as follows;

$$E - \left[\begin{array}{l}\omega_s \text{ increases from zero to 16.9 lb/in} \\ C_1 \text{ decreases from 50 to zero ppm}\end{array}\right.$$

$$T - \left[\begin{array}{l}\omega_s \text{ decreases from 12.8 to 1.2 lb/in} \\ C_2 \text{ increases from 181 to 230 ppm}\end{array}\right.$$

$$P - \left[\begin{array}{l}\omega_s \text{ increases from 0.18 to 0.20 lb/in} \\ C_3 \text{ increases from 268 to 269 ppm}\end{array}\right.$$

To estimate the quantities of E, T and P adsorbed in Zone 2, several simplifying assumptions were made. It was assumed that L_z is determined by the strongest adsorbed vapor, in this case E, and that L_z is the same in adsorption of mixtures as when E is adsorbed singly. The second assumption is that the factor

$$\left[\frac{\omega_s-\omega_z}{\omega_s}\right] = 0.77$$

from Equation 4-26 applies to vapor E. The third assumption is that for T and P

$$\left[\frac{\omega_s-\omega_z}{\omega_s}\right] = 0.23$$

Pounds E adsorbed in Zone 2

From Figure 4-17, L_z is 3.6 in. at U = 110 ft/min and V = 135 cm³/mol. Using the first factor above ω_z = 3.9 lb/in average when ω_s = 16.9 lb/in. The total amount E adsorbed in

Zone 2 is then

$$3.6 \times 3.9 = \underline{14.0\ \text{lb}}$$

Pounds T adsorbed in Zone 2

Using the second factor above, ω_Z = 9.86 lb/in average when ω_S = 12.8 lb/in. The total amount of T adsorbed in Zone 2 is then

$$3.6 \times 9.86 = \underline{35.5\ \text{lb}}$$

Pounds P adsorbed in Zone 2

Using the second factor above, ω_Z = 0.14 lb/in average when ω_S = 0.18 lb/in. The total amount of P adsorbed in Zone 2 is then

$$3.6 \times 0.14 = \underline{0.50\ \text{lb}}$$

The situation is analogous in Zone 4. L_Z is determined by vapor T and is 3.3 in. when U = 110 ft/min and V = 106 cm^3/mol.

Pounds T adsorbed in Zone 4

ω_Z = 2.95 lb/in average when ω_S = 12.8 lb/in, and total amount adsorbed is

$$3.3 \times 2.95 = \underline{9.7\ \text{lb}}$$

Pounds P adsorbed in Zone 4

ω_Z = 3.55 lb/in average when ω_S = 4.60 lb/in, and total amount adsorbed is

$$3.3 \times 3.55 = \underline{11.7\ \text{lb}}$$

Profile of adsorbed E

Total amount adsorbed		24.2 lb(1)
Amount in Zone 2		14.0
Amount in Zone 1		10.2 lb
Length of Zone 1 [10.2/16.9]	0.60 in	

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(1) See page E-13

Length of Zone 2	3.6 in		

Profile of adsorbed T

Total amount adsorbed			61.2 lb
Amount in Zone 1 [1.2 x 0.60]		0.7	
Amount in Zone 2		35.5	
Amount in Zone 4		9.7	45.9
Amount in Zone 3			15.3 lb
Length of Zone 3 [15.3/12.8]	1.2 in		
Length of Zone 4	3.3 in		

Profile of adsorbed P

Total amount adsorbed			57.0 lb(1)
Amount in Zone 1 [0.05 x 0.60]		0.03	
Amount in Zone 2		0.50	
Amount in Zone 3 [0.18 x 1.2]		0.22	
Amount in Zone 4		11.7	
Amount in Zone 6		3.1	15.5
Amount in Zone 5			41.5 lb
Length of Zone 5 [41.5/4.60]	9.0 in		
Length of Zone 6	2.9 in		

Total length of carbon bed

Zone	L, in
1	0.6
2	3.6
3	1.2
4	3.3
5	9.0
6	2.9
Total	20.6 in

The shape of the adsorption front profile for E in Zone 2, T in Zone 4 and P in Zone 6 is assumed to be identical to the vapor-phase curve as calculated from log $[C_i/C]$ in

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(1) See page E-13

Equation 4-28. In these calculations

$$L = k \log [\omega_s/\omega] \Big]_{\omega = 0.01\,\omega_s,}^{\omega = \omega_s}$$

$L = 0$ when $\omega_s/\omega = 1.0$ and

$L = L_z$ when $\omega_s/\omega = 100.$

For the desorption profiles of T and P in Zone 2 and P in Zone 4,

$$L = -k \log [\omega_s/(\omega_s-\omega_i)] + k \log [\omega_s/(\omega_s-\omega)] \Big]_{\omega = \omega_i}^{\omega = 0.99\,\omega_s}$$

Here ω_i is the amount adsorbed per inch of bed length in the previous zone. At

$$\omega = 0.99\,\omega_s,\ L = L_z$$

Estimate of Secondary Adsorber Size for Gas Regeneration with Secondary Adsorption System

The following is a sample calculation for estimating the size of the secondary adsorber for a carbon-resorb system utilizing gas regeneration and recovery of desorbed solvent or pollutant by means of a secondary adsorber, page 6-40. The bed is to be sized to give a steam-to-solvent ratio of 6.0.

Bases for Calculations

Primary Adsorber Effluent

Pollutant = 4-methyl-2-pentanone
F = 306 ft^3/min (at 298°K)
C_e = 4,000 ppm; 1.02×10^{-3} lb/ft^3
T = 302°F; 423°K
t = 120 min

Secondary Adsorber Influent

Same as above except T = 298°K

Secondary Adsorber

Carbon = BPL V Type
Mesh size = 4 to 10; D_p = 0.35
Density (d) = 31.2 lb/ft^3; 2.6 lb/in. per ft^2
L = 20 in.

Bed length L of 20 in. was selected as the fixed bed dimension because the preliminary calculation showed that the bed diameter would be near 24 in. A 20 in. bed length is a reasonable dimension with a 24 in. diameter. Also, regeneration calculations that had already been made apply most accurately to 20 in. bed lengths.

The equation used for the estimate is Equation 4-23, reproduced below:

$$t_b = \frac{A_c}{FC_i} [\omega_s L_s + \omega_z L_z].$$

The above equation was modified for this application and has the form

$$t = \frac{A_c d \Delta\omega}{FC_i} \; [L_s + 0.23\, L_z]$$

where t = 120 min, regeneration time
L = $L_s + L_z$, in.
d = 2.6 lb/in. per ft²
A_c = bed area, ft²
$\Delta\omega$ = $\omega_s - \omega_r$, operating capacity, lb/lb
ω_z = $0.23\ \Delta\omega$

With the above known values substituted into the above equation, it now has the form

$$14.1 = A_c \Delta\omega [L_s + 0.23\, L_z]$$

To determine $\Delta\omega$ for a steam-to-solvent ratio of 6.0, it is first necessary to determine ω_s, using Equation 4-19 and Curve V of Figure 4-12. In Equation 4-19 $V = V_m = 140$ cm³liq/mol, $p_o = 9470$ ppm and $p = 4000$ ppm. $A = 0.8$ and from Curve V, $\omega_s = 0.44$ cm³liq/g or 0.31 lb/lb. From a curve of type shown in Figures 4-22, -23 and -24 it is now necessary to find a ω_r that will give a steam-to-solvent ratio of 6.0, according to the following equation

$$\frac{\text{lb steam/lb carbon}}{\omega_s - \omega_r} = 6.0.$$

At $\omega_r = 0.17$, lb steam/lb carbon is 0.85 which gives a steam-to-solvent ratio of 6.0 at $\Delta\omega = 0.14$ lb/lb. Now

$$100 = A_c\, [L_s + 0.23\, L_z].$$

L_z depends on $U = F/A_c$. From Figure 4-17, L_z can be determined for various U at $D_p = 0.35$ cm and $V = 125$ cm³liq/mol for 4-methyl-2-pentanone. The conditions of the above equation are satisfied when

U = 54.5 ft/min
L_z = 2.5 in.
A_c = 5.5 ft²
L_s = 17.5 in.

The volume of carbon is 9.2 ft^3 and weight is 290 lb.

For the 37.5 lb solvent adsorbed by the 290 lb, the overall operating capacity is 0.13 lb/lb compared to 0.14 lb/lb where the adsorption is more correctly distributed over the saturated and adsorption zone bed lengths.

Calculations on Carbon-Resorb with Gas Regeneration, Condensation and Vapor Recycle

These calculations estimate the number of cycles to attain steady state, and, after the steady state is attained, estimate the flow rates and concentrations to the on-stream adsorber and to the condenser and the weight of vapor recycled when condenser is operated at 32°F. For purpose of calculations refer to page 6-44.

Fixed Parameters

Pollutant or solvent vapor - 4-methyl-2-pentanone
Carbon type - BPLV
Carbon mesh size - 4 to 10 U.S. std sieve
Carbon density = 31.2 lb/ft^3
t_b, service time = 82 hr
t, regeneration time = 120 min
A_c = 27.2 ft^2
L_t = 21.3 in.

Weight of carbon for each inch of bed depth is 71 lb. The regeneration starts on the 80th hr of service time and terminates on the 82nd.

First Cycle Adsorption Phase

F to adsorber = 3,000 ft^3/min
C_i to adsorber = 10 ppm; 2.55×10^{-6} lb/ft^3
T = 77°F; 298°K

First Cycle Regeneration Phase

F to condenser = 306 ft^3/min @ 77°F
C_e to condenser = 4000 ppm; 1.02×10^{-3} lb/ft^3

Saturation vapor concentration at 32°F for 4-methyl-2-pentanone is 0.44×10^{-3} lb/ft^3.

Amount removed by the condenser, at 100% efficiency, is:

Concentration in gas stream at 32°F = 1.11×10^{-3} lb/ft^3
Saturation concentration at 32°F = $\underline{0.44 \times 10^{-3}}$
Amount condensed = 0.67×10^{-3} lb/ft^3,

$$306\ [273/298] \times 0.67 \times 10^{-3} = 0.188\ \text{lb/min},$$

$$120\ \text{min} \times 0.188 = \underline{22.6\ \text{lb}}.$$

Since 37.5 lb must be condensed, the process has not come to a steady state.

The total weight recycled is

$$306\ [273/298] \times 120 \times 0.44 \times 10^{-3} = 14.7\ \text{lb}.$$

Second Cycle Adsorption Phase

The rate of recycle to the impure airstream (during regeneration) is

$$306\ [273/298] \times 0.44 \times 10^{-3} = 0.123\ \text{lb/min}.$$

The rate of outside vapor input to the impure airstream is

$$3000 \times 10 \times 10^{-6}\ [100/392] = 0.0076\ \text{lb/min},$$

where 392 is the molar volume of air in ft^3 at 77°F and 100 is the molar weight of 4-methyl-2-pentanone. The total vapor input rate (during regeneration) is

$$0.1230 + 0.0076 = 0.131\ \text{lb/min},$$

The total flow rate to the adsorber (during regeneration) is

$$3000 + 306 = 3306\ \text{ft}^3/\text{min}.$$

The influent concentration (during regeneration) is

$$[0.131/3306] \times [392/100] \times 10^{6} = 155\ \text{ppm}.$$

Second Cycle Regeneration Phase

It requires a slightly larger amount of regenerating gas to regenerate the carbon bed on the second cycle than on the first. The new figure for F to condenser is 313 ft^3/min at 77°F.

The amount desorbed is 37.5 lb brought in from the outside and the 14.7 lb recycled. The concentration C_e to condenser is

[37.5 + 14.7] [313 x 120] = 1.39 x 10^{-3} lb/ft^3; 5440 ppm

Amount removed by the condenser, at 100% efficiency, is:

Concentration in gas stream at 32°F = 1.52 x 10^{-3} lb/ft^3
Saturation concentration at 32°F = 0.44 x 10^{-3}
Amount condensed = 1.08 x 10^{-3} lb/ft^3,

313 [273/298] x 1.08 x 10^{-3} = 0.310 lb/min,

120 min x 0.310 = 37.1 lb.

Since 37.5 lb must be condensed, the process has virtually come to a steady state. The total weight recycled is

313 [273/298] x 120 x 0.44 x 10^{-3} = 15.1 lb.

Third Cycle Adsorption Phase

The rate of recycle to the impure airstream (during regeneration) is

313 (273/298] x 0.44 x 10^{-3} = 0.126 lb/min,

The total vapor input rate (during regeneration) is

0.126 + 0.0076 = 0.134 lb/min

The total flow rate to the adsorber (during regeneration) is

3000 + 313 = 3313 ft^3/min.

The influent concentration (during regeneration) is

[0.134/3313] x [392/100] x 10^6 = 158 ppm

Third Cycle Regeneration Phase

The required increase in the amount of regenerating gas is nil. F to condenser = 313 ft^3/min at 77°F.

The amount desorbed is 37.5 lb brought in from the outside and 15.1 lb recycled. The concentration C_e to condenser is

$[37.5 + 15.1] [313 \times 120] = 1.40 \times 10^{-3}$ lb/ft^3; 5500 ppm.

Amount removed by the condenser, at 100% efficiency, is:

Concentration in gas stream at 32°F = 1.53×10^{-3} lb/ft^3
Saturation concentration at 32°F = $\underline{0.44 \times 10^{-3}}$
Amount condensed = 1.09×10^{-3} lb/ft^3

$313 [273/298] \times 1.09 \times 10^{-3} = 0.312$ lb/min,

120 min x 0.312 = 37.5 lb.

Since 37.5 lb must be condensed, the process is at steady state.

At steady state operation the following conditions prevail, measured at 77°F:

F to adsorber = 3313 ft^3/min
C_i to adsorber = 158 ppm
F to condenser = 313 ft^3/min
C_e to condenser = 5500 ppm

Weight of vapor recycled/cycle = 15.1 lb

Weight of vapor condensed/cycle = 37.5 lb

Calculation of Service Times for Multistage with Displacement of Beds

(from page 6-49)

These calculations are for the T. Melshime type system. Two organic compounds, 4-methyl-2-pentanone and propanone, are used to represent the range of pollutants that might be encountered. Service times are calculated for three influent concentrations, 1.0, 10, and 100 ppm.

Fixed Parameters

Carbon type = BPL V
Carbon mesh size = 4 to 10 U.S. std sieve
Carbon density = 31.2 lb/ft³
A_c, bed area = 82 ft²
L_t, total bed length = 16 in.
F, flow = 10,000 ft³/min
d, carbon density = 2.6 lb/in. per ft²
T, adsorption temp. = 298°K

Equation for the Calculations

A modified form of Equation 4-23 was used in the calculations. After the first displacement of the carbon beds, no consideration need be given to the amount adsorbed in the adsorption zone since it is always displaced into the second stage. The equation now has the form

$$t = \frac{\omega_s A_c d}{F C_i} L_t, \quad (1)$$

or with fixed parameter substituted,

$$t = 0.341 [\omega_s / C_i] \quad (2)$$

Calculated Results

The following tables summarize the results of the calculations. ω_s was determined for each C_i using mathematical term 4-19, and the generalized adsorption curve given in Figure 4-12.

	C_i, lb/ft³	
C_i, ppm	4-methyl-2-pentanone	propanone
1	2.55×10^{-7}	1.48×10^{-7}
10	2.55×10^{-6}	1.48×10^{-6}
100	2.55×10^{-5}	1.48×10^{-5}

	4-methyl-2-pentanone		propanone	
C_i, ppm	ω_s, lb/lb	t, hr	ω_s, lb/lb	t, hr
1	0.11	2450	0.0047	180
10	0.16	360	0.013	50
100	0.20	45	0.034	13

Appendix F

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Appendix G

Introduction to the Bibliography

Information sources considered pertinent to the Package Sorption Device Study are included in the subsequent bibliography. Important sources include technical literature, related government contract or in-house studies, trade publications and data obtained by letter or interviews.

The bibliography has been divided into subsections with references in each subsection placed in alphabetical order by author. This was done in order to make it easier to locate cited references and additional collateral information. The sections are titled and self-explanatory.

In the text of the report, the author or principal investigator is named first followed by the year the article was published. In the bibliography the major author's name appears first in the same way it appeared in the text. This is followed by additional information needed to clarify and enable the reader to locate the article. The year of publication is enclosed by parenthesis at the end. Often the author is unknown, an article may be published by a government agency, professional or trade society, or in some other manner. In these cases the key word and date of publication are used in the text. Abbreviations are sometimes used, again followed by the year of publication. Key words or abbreviations appear the same way in the bibliography followed by additional identifying information spelling out the abbreviation.

The titles of periodicals, serials and non-serial publications are abbreviated in the bibliography according to the "American Standard for Periodical Title Abbreviations", and can be located in Chemical Abstracts.

Appendix G

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